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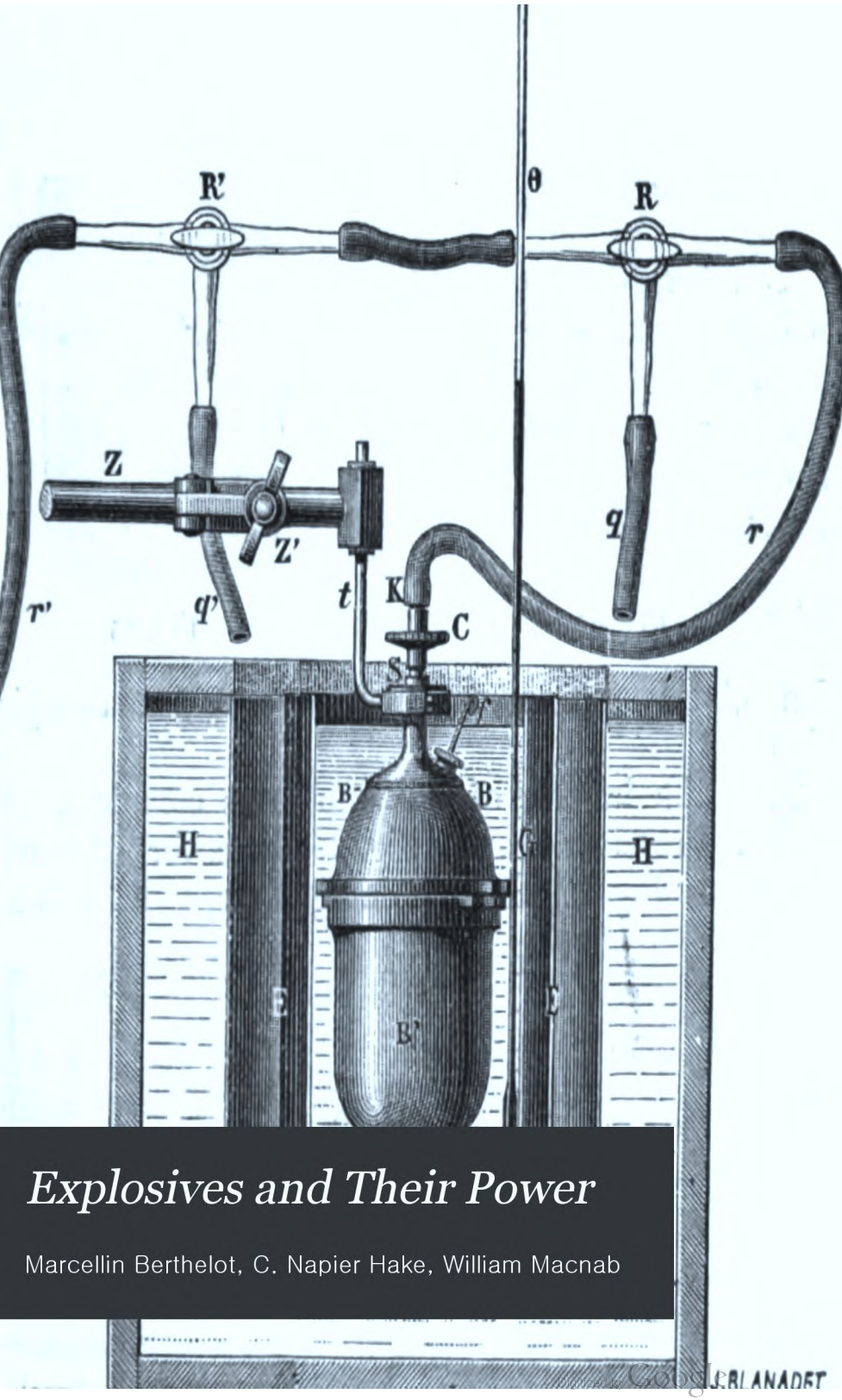

Explosives and Their Power

Marcellin Berthelot, C. Napier Hake, William Macnab

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EXPLOSIVES

AND THEIR POWER.

TRANSLATED AND CONDENSED FROM THE FRENCH

OF

M. BERTHELOT

By C. NAPIER HAKE,

FELLOW OF THE INSTITUTE OF CHEMISTRY, INSPECTOR OF EXPLOSIVES TO THE GOVERNMENT OF VICTORIA;

AND WILLIAM MACNAB,

FELLOW OF THE INSTITUTE OF CHEMISTRY.

WITH A PREFACE BY

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WITH ILLUSTRATIONS.

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PREFACE.

THE great work of M. Berthelot has for some years been a mine from which copious stores of valuable matter have been obtained and translated into various languages.

So far, however, no English translation or adaptation of the book, as a whole, has appeared.

The idea of making such a translation, or, rather, condensation, of M. Berthelot's somewhat bulky volumes occurred some time ago to Mr. Hake and myself. Circumstances, however, notably the appointment of Mr. Hake to the Inspectorship of Explosives in the Colony of Victoria, and a considerable pressure on my own time, prevented our carrying out this project in the way originally intended. But Mr. Macnab, then associated with, and subsequently successor to, Mr. Hake in his London business, has undertaken and carried out the larger portion of the very laborious work involved, and thus it is really to his energy and kindness that the work as it now appears is due. M. Berthelot's reputation as a scientist is world-wide; his attention was first especially drawn to explosives in the year 1870, and his labours have been continued with little, if any, intermission to the present time.

The great key-note of the work now translated is the application of thermo-chemistry to the study of explosives. Though not the first in this field, yet M. Berthelot has, in the extent and variety of his researches, eclipsed his colleagues, and it is mainly due to him that thermo-chemistry occupies the position which it now holds in this department of science.

The book does not pretend to be a practical guide to manufacture, but is, on the other hand, most valuable to the

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manufacturer and practical experimentalist in the indications which it gives of the properties and powers likely to be possessed by an explosive already made, or by one in contemplation.

Scores of useless and dangerous mixtures would never have seen the light had the inventors known and profited by what M. Berthelot has told us.

Since the publication of M. Berthelot's work, new explosives have come prominently on the scene both for military and civil purposes.

Perhaps the most noteworthy of these are the various so-called "flameless" and "smokeless" explosives. To the first of these belongs a group, whose main constituents are nitrate of ammonium mixed with dinitrobenzol, or other nitro-derivative of the benzol series. Such are Roburite, Bellite, Securite, and Ammonite, all of which are in use in this country for blasting purposes, especially in fiery mines. To the second class belongs the very numerous but not very varied group of "smokeless" or quasi-smokeless powders. Of these, one or another has been adopted by most nations for military purposes. They are divisible into two distinct classes, viz. those which consist of nitrocellulose as their main constituent, and those which have not only nitrocellulose, but nitroglycerin as their principal constituents.

To these two classes they all practically belong up to the present time, though there are almost innumerable variations in added ingredients or details of manufacture. By far the oldest is the simple nitrocellulose powder. Some forms of it have been widely used for many years in the sporting world. The older powders, however, though excellent for shot-guns, failed in the uniformity of result so essential in a military arm, and the difficulties have been but comparatively recently overcome.

The close attention which has been paid of late years to the subject of explosives has not been without its effect on the oldest of them. Gunpowder, not so very long ago a somewhat haphazard mixture, has been made to take its place as an explosive deserving and obtaining at least as much care in its manufacture and treatment as the so-called "chemical explosives."

Picric acid, too, under various names and in various shapes, has advanced from the rank of a useful article of ordinary commerce to that of a powerful destructive agent.

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But of all these recent advances the germs may be found in M. Berthelot's work, not necessarily in all cases originated by him, but more or less worked out, examined, and compared, and having, so to speak, the soil prepared for their subsequent growth. As previously stated, a certain amount of omission and condensation has been exercised, for the original volumes consist rather of a series of essays than one connected work, and this condensation became, to avoid repetition, not only advisable, but necessary. Several portions, consisting of matter of merely historical interest, such as the history and origin of explosives, and the history of methods of extraction of saltpetre in France, have been omitted.

M. Berthelot adheres to the older chemical notation; this has been replaced by that more recently introduced and now most commonly in use.

It should be added that this book has been produced with the full consent of M. Berthelot, who has also suggested what Mr. Macnab has carried out, viz. the addition of abstracts of some of M. Berthelot's essays published since the appearance of the main work, and principally relating to the propagation of detonation in explosive gaseous mixtures, with further studies on the "explosive wave" in solid and liquid bodies.

J. P. C.

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ERRATA.

Page 124, *add*, "The large calorie is the unit employed, and the equivalents represent grams."

„ 160, line 7, *for* "these two substances" *read* "nitre and other compounds containing oxygen."

„ 288, line 2 from bottom, *for* "carbon monnade" *read* "carbonic oxide."

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EXPLOSIVES AND THEIR POWER.

BOOK I.

GENERAL PRINCIPLES.

CHAPTER I.

FORCE OF EXPLOSIVES IN GENERAL.

THE force of explosive substances is expressed by the pressure which they exert, and by the work which they accomplish. In a confined space, pressure results in the simple rending of the envelope, without any subsequent work being effected. This is exemplified by the fracture of a shell, through the freezing of water contained in it, or the splitting of a rock by hydraulic wedges. The effect of an explosive would be to disperse the fragments of the shell, or to pulverise or displace the rock. This subsequent action represents the mechanical work of the explosive substance.

The pressure is due to the gases evolved, and is dependent on their volume and temperature. The work done depends principally on the amount of heat disengaged, which is a measure of the energy developed.

In other words, the maximum work that an explosive substance is capable of producing, is proportionate to the amount of heat disengaged during its chemical transformation.

This may be expressed in kilogrammetres by the formula 425 Q, where Q is the number of units of heat evolved.

This theoretical limit is never reached in practice, but still a knowledge of it is indispensable, as it is the only absolute point of comparison.

The effective transformation of this energy into work, depends on the volume of the gases evolved, the amount of heat generated, and on the law of expansion.

A fraction only of the energy can be actually realized in

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practice, in the form of useful work, a considerable amount being absorbed in heating the surrounding medium, in creating in it wave-motion, and in various other ways. For instance, in blasting rock, the useful work consists partly in shattering the rock, and partly in displacing the shattered masses. The remaining energy is absorbed by work, owing to (1) incomplete combustion, (2) compression and chemical changes induced in the surrounding material operated on, (3) energy expended in the cracking and heating of the material which is not displaced, (4) the escape of gas through the holes and fissures caused by the explosion.

The calculation of the distribution of the energy of an explosive between the mechanical work accomplished, the heating of the surrounding medium, and the vibratory movement communicated to the ground or air, etc., is very complicated, and will be treated of in a later portion of this work.

A knowledge of the special properties of explosives enables us to judge, more or less, which particular explosive is likely to be suitable for a particular class of work. In popular language, they are divided into "High" and "Low," and of these two classes, Dynamite and Gunpowder may be taken as the particular types, but no hard and fast line can be drawn between them.

Generally speaking, we mean by "high" explosives, those in which the chemical transformation is very rapid, and which exert a crushing or shattering effect; a comparatively slow chemical transformation and propelling effect being, on the other hand, characteristic of a "low" explosive.

In mercury fulminate we have an extreme instance of rapid chemical transformation, accompanied by intense local action, and other phenomena common to this class of explosives.

The more common "high" explosives are bodies containing a large amount of oxygen, and possessing a definite chemical composition.

They are produced by the action of nitric acid on organic substances forming nitric ethers (nitroglycerin, nitromannite) or nitro-substitution compounds (picric acid and its derivatives).

In consequence of the intimate contact of the combustible and the oxygen in such compounds, a more energetic and rapid action is developed on explosion than that which would result from a simple mixture.

Perchloric ethers and mercury oxycyanide produce analogous effects, as also ammonium nitrate, bichromate and perchlorate (under certain conditions), the acid giving up its oxygen, and the ammonia its hydrogen.

Formerly the force of an explosive was deduced from the weight of available oxygen which it contained; but this idea is inaccurate, for oxygen does not necessarily enter into the

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composition of an explosive substance. Take, for instance, diazobenzol and nitrogen sulphide or chloride, bodies which are formed with absorption of heat from their elements, and which decompose with a reverse thermal action.

An explosive compound may be employed either in a pure state or mixed with an inert substance, as in the case of dynamite, a mixture of silicious earth and nitroglycerin.

The effect of such mixture is to diminish the violence of the explosion, and to give to it a propelling or rending action rather than a shattering one.

Or an explosive compound may be mixed with a substance which increases the force of the explosion, as in the case of nitroglycerin mixed with an active base. And here it is well to distinguish three fundamental cases, based on the relation between the oxygen and the combustible elements in the explosive body.

This relation is either that of a total combustion, as in the case of silver oxalate, resolvable by the explosion into carbonic acid and metallic silver.

$$C_2Ag_2O_4 = 2CO_2 + Ag_2.$$

Or the oxygen is deficient, which is the case in potassium picrate and in gun-cotton.

Or, on the contrary, the oxygen is in excess; which is the case in nitromannite and nitroglycerin.

In the last case there may be an advantage in utilising the whole energy of the explosive body by adding a combustible such as carbon, or better, nitrocotton, an explosive in itself, in suitable proportions.

In the second case, where there is a deficiency of oxygen, an oxidising agent such as potassium nitrate, may be added to the explosive.

Mixtures, however, in which total combustion takes place are not always those which produce the greatest effect in a given weight and under given conditions.

Gunpowder, for example, mixed with a quantity of nitre sufficient for complete combustion, develops, weight for weight, less gas, and consequently less pressure, and produces less effect than ordinary powder, in which there is a deficiency of oxygen.

The effects which result from the substitution of one salt for an equivalent salt, in explosive mixtures, deserve particular attention. Let us confine ourselves to the nitrates and to a simple substitution which does not change the nature of the powder; for instance, sodium nitrate, or barium nitrate, for potassium nitrate.

The substituted salt, in equivalent proportions, would hardly change the amount of heat liberated nor the volume of the gases in the case of total combustion.

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But, supposing even that in an incomplete combustion, such as that of gunpowder, no change in the chemical reactions were produced, nevertheless the substitution of barium nitrate for potassium nitrate would result in an increase of the absolute weight of the mixtures, and consequently diminished pressure and less heat evolved per kilogramme, for the reason that the equivalent of potassium nitrate, KNO_3 being 101, and that of barium nitrate 130·5, the weight of the oxidising agent necessary to burn a given weight of combustible is increased one-third.

The equivalent of sodium nitrate, $NaNO_3$, being 85, there will be a less weight of it required than of potassium nitrate.

The heat set free by this weight, which supplies an equal amount of oxygen to the combustible, is, moreover, about the same.

The substitution of sodium nitrate for potassium nitrate is therefore advantageous in this respect. Unfortunately, the hygroscopic properties of sodium nitrate are against its general application.

Copper nitrate, $Cu(NO_3)_2$, would doubtless be preferable to any other, because its equivalent is a little less than that of potassium nitrate, and more especially as this salt, in its equivalent proportions, supplies to the combustible bodies a fifth more oxygen than the alkaline nitrates, in consequence of the total reduction of the copper. This deserves attention, for potassium, sodium, and barium remain after the explosion in the state of carbonates. By reason of this twofold circumstance, viz. the lesser equivalent and the larger proportion of oxygen available, the heat developed by the same weight of copper nitrate in burning the same combustible is considerably in excess of that produced by the alkaline salts. Unfortunately, copper nitrate has such a strong affinity for water that it has hitherto been found impossible to obtain it in the anhydrous form.

Lead nitrate, $Pb(NO_3)_2$, and silver nitrate, $AgNO_3$, are, on the contrary, easy to obtain anhydrous, and offer as oxidising agents advantages equal, if not superior, to those of copper nitrate when employed in equivalent proportions.

But weight for weight this advantage no longer exists, because their equivalents (165·5 and 171) are too high. The price of silver nitrate would, moreover, militate against its general adoption, and lead nitrate gives off very dangerous fumes in confined places.

It has been considered advisable to enter into these details in order to show what a variety of conditions have to be considered in order to produce an explosive applicable to a particular class of work, and in which the nature and proportions of the constituents are such as to develop the maximum effect. In order to work successfully to this end it is necessary that all experiments should be directed by certain laws deduced from chemical and dynamical considerations.

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CHAPTER II.

1. CHEMICAL COMPOSITION.

1. THE composition of the products of explosion can be foreseen whenever the explosive substance contains enough oxygen to transform the elements into stable compounds, and at the highest degree of oxidation, as in the case of nitroglycerin and nitromannite. This limit corresponds also to the maximum thermal effect. It is not always attained in practice, especially by the mixtures which contain potassium nitrate, on account of the rapidity of the chemical and mechanical reactions and of the cooling.

The explosive decomposition of certain binary compounds, such as nitrogen sulphide, gives rise also to known products.

2. On the contrary, when the oxygen does not suffice for total oxidation, or when ternary substances (not containing oxygen), such as diazobenzol, are in question, the products formed generally vary with the conditions of the explosion, temperature, pressure, expansion, mechanical effects, etc. This is also the case with black powder, gun-cotton and potassium picrate.

Under these circumstances, the composition of the products cannot be determined beforehand, but must be ascertained by special analyses, and for each condition of the reaction.

3. In this connection, experiments may be given relative to the influence of the initial temperature and the rapidity of heating on the mode of decomposition of bodies, and especially the seven different modes of the decomposition (some endothermal, others exothermal) of ammonium nitrate, a definite compound, which leads to more decisive conclusions than simple mixtures.

4. The following are the seven different modes of decomposition which ammonium nitrate undergoes.

(*a*) The dissociation or partial decomposition of fused or even gaseous ammonium nitrate into gaseous nitric acid and ammonia, which seems to be first produced and at a low temperature. It corresponds necessarily with absorption of heat, namely,

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− 41,300 cal. when the solid nitrate is used, and about − 37,000 when the salt is fused.

(*b*) The formation of nitrogen monoxide from ammonium nitrate at a higher temperature, and when the heat is carefully regulated. The reaction : NH_4NO_3 (solid) = N_2O + $2H_2O$ (gas) develops + 10,200 cal., the fused salt about + 14,000 cal.

If the salt be supposed to be previously decomposed into gaseous nitric acid and ammonia, and the action to have really taken place between these two compounds, the formation of nitrogen monoxide, HNO_3 gas + NH_3 = N_2O + $2H_2O$, would develop + 51,500 cal.

(*c*) When rapidly heated, the explosive decompositions, properly so called, of ammonium nitrate take place; one of them produces nitrogen and oxygen.

$$NH_4NO_3 = N_2 + O + 2H_2O \text{ (gas)}.$$

This reaction develops from the solid salt + 30,700 cal.; from the fused salt, about + 35,000 cal.

(*d*) Nitrogen and nitrogen dioxide are also formed—

$$2NH_4NO_3 = N_2O_3 + N_2 + 4H_2O,$$

and + 9200 cal. are given off when the salt is solid and about + 13,000 cal. when it is fused.

(*e*) Heat is also liberated when ammonium nitrate gives rise to nitrogen, water and nitrogen tetroxide—

$$4NH_4NO_3 = 3N_2 + N_2O_4 + 8H_2O$$

+ 29,500 cal. being set free from the solid salt, and + 33,500 cal. from the fused salt.

(*f*) The ammonium nitrate may also be conceived as being transformed into nitrogen, water and nitrogen trioxide.

$$3HN_4NO_3 = 2N_2 + N_2O_3 + 6H_2O.$$

This reaction liberates + 23,300 cal. from the solid salt, and about + 27,000 cal. from the fused; but never takes place alone, as nitrogen trioxide exists only in the dissociated state in presence of nitrogen dioxide and nitrogen tetroxide.

(*g*) Lastly, ammonium nitrate can be resolved into gaseous nitric acid, nitrogen and aqueous vapour under certain influences such as spongy platinum.

$$5NH_4NO_3 = 2HNO_3 + 4N_2 + 9H_2O$$

yielding + 33,400 cal. from the solid salt, and about + 37,500 cal. from the fused.

These different modes of decomposition of ammonium nitrate, which may be distinct or simultaneous, or more exactly the predominance of any one of them, depend on their relative rapidity and on the temperature at which decomposition is produced. This temperature is not fixed, but is itself subordinate to the rapidity of heating. It has been established by a great

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number of observations, that each mode of decomposition of a given substance commences at a certain temperature, and in a given time a limited weight of substance is decomposed.

Special stress is laid upon the singular property which ammonium nitrate possesses of undergoing several distinct modes of decomposition, according to the rapidity of heating and the temperature to which the substance is raised. Of these decompositions, some take place with liberation of heat, others with absorption of heat.

5. A similar property is possessed by most bodies which liberate heat during decomposition, and especially by explosive bodies, properly so called. It is particularly manifested in proportion to the difference of the local conditions developed by progressive heating in a mass which is not instantaneously decomposed.

On the other hand, the sudden explosion of detonating substances, when they consist of a definite compound such as gun-cotton, nitroglycerin, mercury fulminate, etc., and when the explosion is readily brought about, the reaction being uniformly distributed throughout the entire mass, appears likely, generally speaking, to give rise to simple and stable products. The extreme conditions of temperature and molecular vibration which accompany the phenomena hardly allow of its being otherwise in a molecularly homogeneous mass.

This is, in fact, what has been verified during the explosion of gun-cotton, as studied by Sarrau and Vieille.

If previous observers have noticed more complicated decompositions, it is because the conditions have been such that the mass underwent partial coolings, and was decomposed at certain points by distillation rather than by true explosion.

From researches made in conjunction with Vieille on the explosion of mercury fulminate, it has been established that this substance is also decomposed in the most simple manner into carbonic oxide, nitrogen, and mercury. With gunpowder the diversity of local conditions of combustion cannot, under any circumstances, be avoided, because a mechanical mixture of three pulverised bodies can never attain the same degree of homogeneousness as a true chemical combination.

6. However, each of the products of the explosion is none the less formed according to a regular law; all result, in short from a small number of definite transformations occurring at various points of the mixture, and the diversity of which is the consequence of the variety of the local conditions.

If the products remained in contact for a sufficient time, they would undergo reciprocal actions, which would bring them to the state corresponding to the maximum heat liberated (at the temperature and under the same conditions of the experiment); but the sudden cooling which they experience prevents this state from being realised.

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The mode of expansion, the nature of the work accomplished, and the more or less complete transformation of the heat into work at the moment of explosion must necessarily play an important part in this connection.

This diversity in the products helps to explain the very varied effects which the explosion of one and the same body may produce, according to the method of inflammation.

2. DISSOCIATION.

1. In order to have a clearer idea of the effects produced by explosive substances, it is necessary to examine not only the products obtained after cooling, but also those which are produced during the explosion, and starting from the moment when the system reaches the maximum temperature. Now, these first products are sometimes simpler than those which are observed after cooling; they result partly from the formation of a lower compound. For instance, from a polysulphide splitting up into sulphur and monosulphide, and partly from incomplete combination, as in the case of a mixture of water vapour with its elements, hydrogen and oxygen.

In the above connection it is indispensable to take account of the phenomena of dissociation.

The quantities of heat and the gaseous volumes under discussion are calculated at 0° C. and 760 mm. This calculation is admissible for explosive compounds which can be resolved into their elements, such as nitrogen sulphide, or for those which give simple and stable products, such as mercury fulminate, which can be completely decomposed into mercury, nitrogen and carbonic acid. But it is inadmissible when carbonic acid, water vapour, potassium polysulphide, sulphate, or carbonate, etc., are formed. In these cases the compounds probably do not exist as such. At the high temperature developed during the reaction they are, no doubt, replaced either wholly or in part by simple combinations, perhaps even by their elements. Consequently the quantity of heat corresponding to the real reactions is less than the quantity measured or calculated from the products observed after cooling, and lowers the maximum temperature, as well as the corresponding pressure. This last point is worthy of closer examination.

2. The pressure of a gaseous system is always diminished by the fact of dissociation.

At first sight, this would seem to be a paradox, as dissociation has the effect of increasing the volume of gases reduced to 0° and 760 mm., when there has been condensation in the act of combination, as in the formation of water vapour or carbonic acid. But, on closer examination, it will be found that in all known cases of combination accompanied by condensation, the

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heat developed by the reaction is such that it increases the gaseous volume if the reaction take place under constant pressure, it consequently increases the pressure if kept at constant volume. The effects are such that the heat liberated increases the gaseous volume in a proportion greater than the condensation, the latter being calculated upon the hypothesis of a total combination effected at the initial temperature of the system. In other words, the pressure of a gaseous system cannot diminish, generally speaking, through the fact of an exothermal reaction, when it takes place at constant volume, and gives rise only to gaseous products.

But dissociation being an endothermal reaction the increase of gaseous volume due to that action is more than counterbalanced by the diminution of volume due to the absorption of heat, and consequently the pressure can never be increased by dissociation.

3. Let us calculate these changes.

The pressure depends on the temperature developed, and on the state of condensation of the products. Let t be the temperature developed by the real reaction, taking place at a constant volume, and supposing the whole of the heat liberated to have been employed in heating the products. Let V be the sum of the volumes of the gaseous bodies which form part of the initial system, supposing them reduced to 0° and 760 mm.

At the temperature t the final system contains a certain number of gaseous bodies. Further, let V_1 be the reduced volume which these bodies would occupy if they could be brought without change of state to 0° and 760 mm.

The ratio of the reduced volumes $\frac{V_1}{V} = \frac{1}{k}$ expresses the condensation produced by the reaction. It is applicable to every pressure and temperature according to the ordinary laws.

An arithmetical value can easily be found for this ratio for every chemical reaction of which the formulæ are related to the molecular volumes. For example—

$$H_2 + O = H_2O \text{ (gaseous) gives } \frac{1}{k} = \frac{2}{3}$$

$$CO + O = CO_2 \text{ (gaseous) gives } \frac{1}{k} = \frac{2}{3}$$

Now let us calculate the pressure developed during the reaction, occurring at constant volume and at the temperature t; the initial temperature being zero, and the initial pressure h.

Admitting the laws of Mariotte and Gay-Lussac, the pressure will become

$$h \times \frac{1}{k}(1 + at)$$

a being equal to $\frac{1}{273}$, as is known.

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This pressure will be superior to, less than, or equal to, the initial pressure according as $1 + at$ is greater, less than, or equal to k.

We should note that $t = \frac{Q}{c}$; Q being the quantity of heat developed in the reaction and c the mean specific heat of the products between zero and $t°$.

4. Further, the pressure increases if the condensation is *nil*, that is if $k = 1$ (chlorine and hydrogen; combustion of cyanogen by oxygen). It increases especially if expansion occurs, that is when $k < 1$ (combustion of acetylene by oxygen) assuming that Q is positive in every direct and rapid reaction between gaseous bodies.

Now let $k > 1$ this condensation is always comprised between certain limits for definite gaseous compounds, limits such that K = 4, 3, 2, $1\frac{1}{2}$. Hence the fundamental condition,

$$1 + a\frac{Q}{c} < k \text{ or } Q < 273(k - 1)c,$$

a condition which is necessary for a diminution of pressure, cannot be realised except in quite exceptional cases, in which the heat disengaged by an internal reaction is very slight, and beyond the scope of any observed reactions. We can assure ourselves of this by making the calculation by means of the specific heats at constant volume deduced from specific heat at constant pressure which Regnault has determined for many bodies.

5. The calculation may also be made in a more general manner by admitting with M. Clausius that the specific heats at constant volume have an identical value for the atomic weights of the various simple bodies; that this value is equal to 2·4: a number which is found for H = 1, in fact, that it does not change by the fact of combination.

Now, W being the quantity of heat disengaged in a reaction between gaseous bodies in relation to the atomic weights, and M the number of atomic weights which are engaged in the reaction, the pressure will only diminish if we have

$$W < 655M(k - 1).$$

It is easy to see that this condition is not fulfilled in the best known gaseous combinations. In making the calculation, whether by the aid of this formula, or the foregoing, no example has been discovered of diminution of pressure among the numerous reactions which have been examined.

It should be noted that it is sufficient to make the calculation for the supposed total reaction, the result being the same for the supposed partial reaction, that is to say, in the case of dissociation. This can be easily proved, for the uncombined

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portion does not contribute any heat and only operates by the difference between the specific heat of the compounds and the sum of that of the components, a difference which is *nil* according to the hypothesis of Clausius.

6. Without carrying this discussion any further, the following general proposition may be deduced from it relative to chemical combination.

When the heat disengaged in a reaction taking place between gaseous bodies, and with the exclusive formation of gaseous products, is entirely applied to heating the products, then there is always increase of pressure, the volume being constant.

This proposition has very important applications in the study of explosive substances; but, of course, it is applicable only to gases forming gaseous products, for it is evident that the formation of a solid compound from gaseous components would cause a reduction of pressure.

The influence of dissociation being thus marked by a lowering in the pressure of the gaseous systems, it must also be observed that its existence and effect should not be unduly exaggerated; the latter must be less than one would at first suppose on account of certain compensations.

We will dwell a little on this matter on account of its great importance.

7. The actual temperature which is developed in an explosive reaction is in general less than the temperature calculated in accordance with the specific heats of the gas, estimated at about the normal pressure and ordinary temperature, since the specific heat of greatly compressed gases is not constant. In fact, the specific heat of gases formed with condensation increases with the temperature, according to the facts observed by Regnault and M. E. Wiedemann on gaseous carbonic acid and other compound gases. It must also increase with the pressure, at one and the same temperature, in proportion as the gas approaches the liquid state, the specific heat of a liquid being nearly always greater than that of the same body in its gaseous form, at the same temperature. An equal quantity of heat applied to compressed gases, such as those which are produced in explosive phenomena, will therefore produce less rise in temperature than if their specific heat were constant, and equal to that of the same gases at the normal pressure, as is generally assumed in these calculations.

Hence a smaller increase in dissociation, which depends chiefly on the temperature. It is further limited by another circumstance, relative to the pressure developed.

8. Now, the actual pressure is not so much diminished as one might judge from a calculation founded on the ordinary laws of gases, and on the lowering of the theoretical temperature. The laws of Mariotte and of Gay-Lussac are hardly applicable

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in the case of such enormous pressures as those observed in the combustion of powder. With greatly compressed gases the pressure varies with the temperature much more rapidly than would follow from these laws; it approaches the rate observed by physicists in the study of vapours. For a given temperature the pressure is therefore generally higher than that which would be given by calculating according to the ordinary laws of gases. This tends to compensate in the calculation of pressures the contrary influences exercised by the variation in the specific heats.

Now, the phenomena of dissociation depend on the pressure, as well as on the temperature. The state of combination of elements, all things else being equal, is higher as the pressure is greater—a relation which is easily conceived *à priori*, and which is confirmed by experiments relative to the decomposition of acetylene into carbon and hydrogen at different pressures by the electric spark.[1] But the pressures increase with the temperatures, and even much more rapidly, as has just been stated; the decomposing influence of the temperature can therefore be compensated, either wholly or in part, by the opposite influence of pressure.

9. The inverse action of these two classes of phenomena remains such that a substance undergoing transformation at constant volume without loss of heat, will tend towards a certain limiting state; the transformation of the first portions will at first raise the temperature and pressure to the point at which dissociation will limit the phenomenon. This is also a theoretical maximum, since the mass is continually cooled by radiation and conduction. But the greater the mass operated upon, the nearer will this result be approached.

10. The phenomena of dissociation do not only exert their influence on the maximum effort which the explosive substance can develop, but they also come into play during the first period of expansion. In proportion as the gases of the explosive expand in acting on the projectile, they cool, in consequence of which the elements enter into combination in a more complete manner and with the formation of more complicated compounds. From this there results a new disengagement of heat which increases without ceasing during the whole of a period of expansion.

Therefore, in general, the transformation effected in the bore of a cannon cannot be regarded as adiabatic. The temperature of the gases will not be lowered by a quantity any way proportionate to the exterior work done, even independently of the losses of heat due to exterior causes of cooling; seeing that restoration of heat takes place through the chemical reaction, during a considerable period.

[1] "Annales de Chimie et de Physique," 4e série, tom. xviii. p. 196. 1869.

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11. The true pressures will therefore always be greater, except at the commencement, than those calculated from the quantity of heat actually disengaged at the moment of maximum temperature.

On the other hand they will be at first less than the pressure calculated from the quantity of heat observed in the calorimeter at the ordinary temperature. But this latter difference diminishes, and finally disappears altogether in proportion as the volume increases, the reactions becoming more complete. The curve of the true pressures, expressed as a function of the volumes, is at first more drawn out than the curve of the theoretical pressures with which it finally coincides, when the state of combination of the elements has become the same as at the ordinary temperature.

12. To sum up, the quantity of heat and consequently the maximum work which explosive substances can develop while burning in a constant volume, may be calculated independently of the phenomena of dissociation, provided the final state of combination of the elements be exactly defined.

Thus the knowledge of the initial composition, and that of the products determine the potential energy, whilst pressure and expansion are subordinates to dissociation.

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CHAPTER III.

HEAT DISENGAGED.

1. THE total quantity of heat disengaged during an explosive reaction, can be experimentally measured in a calorimeter. The apparatus employed for this purpose will be described further on. The quantity of heat is generally positive. There are, however, certain reactions, such as that of tartaric acid on sodium bicarbonate, which develop gas and at the same time produce cold. The explosion of the containing vessel might thus coincide with the latter phenomena. It would be the same with the explosion of a vessel containing a compressed gas. But these are exceptional cases, and outside of the ordinary applications of explosives.

2. The heat developed can be calculated after deducting the mechanical effects, when the products of the explosive reaction are exactly known, and when the heat of formation of the original substances, as well as of the products, from the elements is also known. It is only necessary to deduct the former quantity of heat from the latter to obtain the heat developed during the explosion.

3. The calculations are made from the thermo-chemical data contained in the tables (pp. 125–144). These tables are taken from the author's "Essai de Mécanique Chimique."

4. The quantity of heat necessary to raise 1 grm. of water from 0° to 1° is generally called a calorie. This unit is everywhere employed to represent the heat disengaged by the transformation of 1 grm. of matter.

But the magnitude of the quantities of heat disengaged when chemical reactions are referred to the equivalent weights (expressed in grms.) has rendered necessary the use of a unit a thousand times greater; this is the large Calorie, the quantity of heat necessary to raise 1 kgm. of water from 0° to 1°.

5. To find, for example, the heat disengaged by the detonation of nitroglycerin, under constant pressure, in the open air,

$$2(C_3H_5N_3O_9) = 6CO_2 + 5H_2O \text{ liquid} + 3N_2 + O.$$

According to the tables, the heat disengaged by the union of

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the elements of nitroglycerin, $C_3 + H_5 + N_3 + O_9 = C_3H_5(NO_3)_3$ liquid, amounts to + 98·0 Cal.

On the other hand, the formation of the products—

$3(C + O_2) = 3CO_2$ disengages	...	...	+ 94 × 3 = 282
$\frac{1}{2}[5(H_2 + O) = 5H_2O]$ „	...	...	+ 34·5 × 5 = 172·5
Total	...	...	... 454·5

The heat disengaged by the explosion will therefore be

$$+ 454{\cdot}5 - 98{\cdot}0 = + 356{\cdot}5 \text{ Cal.}$$

This is the heat set free by the decomposition of one equivalent of nitroglycerin under atmospheric pressure about the temperature of 15°.

6. If the decomposition take place in a closed vessel, under *constant volume*, rather more heat will be set free; because the gases developed by the nitroglycerin in the open air, effect a certain amount of work in driving back the atmosphere, and this work consumes a corresponding amount of heat.

The excess of heat resulting from an explosion in a closed vessel may be calculated by the aid of the following formula:

$$(1) \quad Qtr = Qtp + (N' - N)0{\cdot}54 + 0{\cdot}002t.$$

Qtp expresses the heat disengaged at constant pressure, Qtr the heat disengaged at constant volume, t the surrounding temperature.

N and N′ are defined as follows:—Let l be the number of litres occupied by the original gas in the closed vessel in which the explosion has taken place, the gases assumed to be reduced to 0° and 760 mm., and l' the number of litres occupied by the gases after explosion, reduced to 0° and 760 mm. Replace l by the expression 22·32N, and l' by 22·32N′, in order to compare the volume of the gases with that occupied by 2 grms. of hydrogen H_2, taken as unity, namely 22·32 litres.

The formula (1) establishes a general relation between the heat of the reactions taking place at constant pressure and those in constant volume. The author has demonstrated this in his "Essai de Mécanique Chimique," tom. i. p. 44.

Let this formula be applied to the decomposition of nitroglycerin, this substance being taken at 15°. In this case we may put N = 0.

Hence

$$N' = \frac{3 \times 4 + 5 \times 2 + 3 \times 2 + 1}{4} = \frac{29}{4} = 7{\cdot}25$$

$$Qtr = Qtp + 7{\cdot}25 \times 0{\cdot}54 + 7{\cdot}25 \times 0{\cdot}002 \times 15 = Qtp + 4{\cdot}13 = 360{\cdot}6 \text{ Cal.}$$

This quantity applies to the weight represented by the formula $C_3H_5(NO_3)_3$, namely 227 grms. One grm. will therefore give 1590 small calories.

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This figure is deduced from the heat of formation of water, carbonic acid and nitroglycerin, the latter being taken from the three following data:—the heat of combustion of glycerin, which leads to its heat of formation; the heat of formation of nitric acid; and lastly, the heat disengaged by the action of this acid on the glycerin.

Sarrau and Vieille have measured directly the heat disengaged by the explosion of nitroglycerin in a closed vessel, and have found 1600 cal. for one grm.

The figures 1590 and 1600 have thus been obtained by the two inverse methods just indicated, and they are as concordant as can be expected, taking into consideration the small errors inseparable from all experiments.

7. It should be remarked here, that the quantity of heat disengaged by an explosive is only a fixed quantity, which can be calculated beforehand, when the material undergoes total combustion, otherwise the heat cannot be calculated for lack of knowledge of the products of combustion, for these can vary with the pressure, the manner of ignition, and many other circumstances (pp. 6, 7).

Further, when working with closed vessels, the oxygen of the air contained in the space plays a part when the combustion is incomplete—its effect is greater the smaller the density of charge. Thus, in calorimetric experiments it is advisable to operate in an atmosphere of nitrogen when there is not total combustion. The walls of the vessel, especially when of iron or copper, bear a part in the chemical reaction which has often been overlooked. These metals are oxidised at the expense of the air or of the nitrates, or attacked by the sulphur, etc. Hence there are subsidiary disengagements of heat which affect the determinations. To avoid these troubles the author conducts all his determinations in vessels lined with platinum.

8. In what has preceded it has been supposed that the chemical reaction was not accompanied by any special mechanical effect. But in general the object of explosions is to do certain work; the measure and valuation of this work ought to be made in each particular case. Hence result most important but complicated calculations for the theory of firearms, in which the expansion of the gases plays an important part. Details of these will be found in the memoirs of Sarrau, De Saint Robert, Noble and Abel, Sebert and Hugoniot, and other authorities who have devoted special attention to ballistics.

9. Without any theory the sum of this work might be arrived at by an inverse process, namely, by effecting the explosive reaction in a calorimeter, and measuring the heat disengaged at the instant in which the work is accomplished. The difference between the quantity of heat disengaged in a reaction effected without mechanical effects, and the same reaction with

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mechanical effects, measures the heat consumed by these mechanical effects. But it is not easy to carry out exact calorimetric experiments under these conditions.

10. However, the heat disengaged measures the maximum work which the explosive can accomplish acting under atmospheric pressure. It suffices to multiply this quantity of heat by 425, the mechanical equivalent of it to express this work in kilogrammetres. This is the value of its potential energy.

The potential energy of an explosive must not be confounded, as has sometimes been done, with the heat of combustion of a substance combustible by air or oxygen; for example, in comparing what has been called the potential of coal with the potential of powder. For the energy of the powder is contained entirely in itself, while the energy of coal in combustion resides not in the inflammable body alone, but in a system composed of this body and the air necessary to burn it. Even in the case of an explosive the total heat disengaged at the ordinary temperature is not in general that which regulates the pressure developed at the moment of explosion. This latter quantity of heat corresponds solely to the formation of compounds actually existing at the temperature and in the conditions of the explosion; that is to say, it is subordinate to dissociation. For example, if at the temperature of explosion the carbonic acid is dissociated to the extent of one-third into carbonic oxide and oxygen, it would be necessary to deduct from the heat transformable into work, the heat corresponding to the metamorphosis of this third consisting of carbonic oxide.

11. From what has been said it will be seen that it is very interesting to compare the potential of an explosive with the work which the gases developed by its explosion could accomplish in the case of an indefinite expansion. This point has hitherto only been experimentally studied in the case of powder; the discussion of the results observed would lead to questions in mechanics which are foreign to the chief subject of this book. It will only be added that, according to the most recent experiments—those of Sébert and Hugoniot[1]—the ratio between the total and potential work for powder would be $\frac{134 \text{ kgm.}}{305 \text{ kgm.}}$, or 44 per cent. This ratio coincides approximately with the ratio in weight of gaseous products to the saline products of the explosion. In practice the limit of work which 1 kgm. of powder can effect falls to 90,000 kgms., that is to say, below one-third of its potential energy.

[1] "Mémorial de l'Artillerie de Marine," tom. x. p. 184. 1882.

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CHAPTER IV.

PRESSURE OF GASES.

§ 1. VOLUME OF GASES.

THE volume of gases formed and their temperature determine the pressure developed when the explosive substance is decomposed in a constant volume. M. Berthelot proceeds to show how these various data are obtained, and gives the usual formulæ found in text-books.

§ 2. TEMPERATURE.

1. The temperature developed by an explosive substance can be directly measured, in principle at least. But, as a matter of fact, this measurement, which is exclusively that of very high temperatures, presents extreme difficulties, and there is hardly any known case in which they have been completely surmounted. All that is known is, that the explosion of powder develops a temperature higher than that required for the fusion of platinum, that is to say, than 1775°.

2. The theoretical calculation of the temperature can be performed in the following manner.

The temperature, T, developed in any reaction, such as an explosion, is calculated by dividing the quantity of heat disengaged, Q, by the mean specific heat of the products, c, estimated between T and the surrounding temperature.

$$T = \frac{Q}{c}.$$

This expression is exact, provided the true specific heat be introduced into it, as well as the quantity of heat corresponding to the formation of the products which really exist at the temperature and under the conditions of the explosion.

3. Theory further shows that the heat disengaged, and, consequently, the temperature produced, are independent of the size

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of the receptacle in which the operation has taken place, whenever the chemical reaction remains the same.

Hence it is also the same with the ratio between the initial pressure and the developed pressure at constant volume. This is, in fact, what follows from Joule's law, provided that such a law apply to gases so highly compressed as those with which we are concerned.

4. We will now examine to what degree these various theoretical data are really known.

On the one hand, the products which exist at the maximum temperature, and under the conditions of the explosion, are not necessarily identical with those which are found after cooling. At this high temperature, the component elements can be only partially combined, or transformed into simpler compounds. Therefore the heat disengaged at the moment of the explosion will be diminished. On the other hand, the state of combination is the more advanced, and the dissociation less, as the pressure developed is more considerable. In general, the maximum temperature appears to be very much below the theoretical.

§ 3. Specific Heat.

1. The specific heat of gases, which is the base of all these calculations, requires to be defined. For the sake of greater simplicity, the specific heat really observable, at the ordinary temperature, in products obtained after cooling, is adopted, this specific heat being taken at constant volume, if the reaction take place in a closed receptacle; or at constant pressure, if we operate at atmospheric pressure. The table of these specific heats will be given on pp. 141–143.

2. However, these suppositions are not accurate. The specific heat taken at the ordinary temperature, T, does not remain constant at higher temperatures for compound bodies, whatever be their state; it is not even so for simple bodies in the liquid or solid state. In reality the greater number of these specific heats increase rapidly with the temperature. More especially, the specific heat of gases compressed to several thousand atmospheres, such as results from the explosion of powder or nitroglycerin, is unknown, and it doubtless varies extremely with the temperature and pressure. Its variations should be similar to those of liquids, from which the state of gases so compressed is not very remote. Now, the specific heat of certain liquids, such as alcohol, can be doubled between limits of temperature so little separated as 0° and 150°, according to the experiments of Regnault,[1] and those of Hirn.[2] This is therefore a very uncertain datum.

[1] "Relation des expériences," etc., tom. ii. p. 272. 1862.

[2] "Annales de Chimie et de Physique," 4e série, tom. x. p. 86. 1867.

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3. Attempts have been made to supplement it by an hypothesis more arbitrary, doubtless, but convenient for calculations. This hypothesis consists in regarding all compound bodies as possessing, at a high temperature, a constant specific heat, independent of temperature and pressure, and equal to that of the sum of their gaseous elements, of course at constant volume. This specific heat will be the same, and equal to 4·8 for every gaseous element of a weight such that it occupies the molecular volume taken as unity.

4. The sum of the specific heats can therefore be found by multiplying the sum of the molecular volumes concerned in the reaction by 4·8, and dividing by the unit volume.

§ 4. Pressure.

The pressure developed at the moment of the explosive reaction can either be calculated *a priori*, or directly measured. This subject will be divided into four sections, viz. :—

Direct measurements (1st section).

Calculations (2nd section).

Density of charge and specific pressure (3rd section).

Lastly, the "characteristic product," a term of comparison wholly deduced from purely empirical data.

First Section.—Direct Measurements.

1. Direct measurements are made with the aid of various apparatus, some based on the static, others on the dynamic method, that is, on the study of the law of the movement imparted to a heavy body.

2. The earliest and simplest of all the apparatus is that of Rumford (1792), who experimentally ascertained the weight capable of keeping in equilibrium the pressure of powder gases.[1] The results obtained by this instrument for densities of charge comprised between 0·1 and 0·3 do not greatly deviate from the most recent figures observed by Noble and Abel. Above these densities Rumford's figures are excessive.

3. The Rodman punch (1857) and its modifications, as well as the Uchatius eprouvette (1869), are based on the size of an indent made on a copper disc by a steel punch fitted to a piston acted on by the gases of the explosive substance. In the apparatus of Meudon, successively improved by Colonels Montluisant and Reffye, the "flowing" of a cylindrical mass of lead, thrust by the gases into a conical channel of smaller dimensions, is observed.

The crusher gauge of the English Commission on explosive substances, deduces the pressure from the crushing of a copper

[1] "Traité sur la poudre par Uppman et Meyer traduit et augmenté par Desortiaux," p. 562. 1878.

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cylinder. All these instruments should be checked by comparison, by studying the effects of well-known pressures and drawing up corresponding tables.

4. The spring dynamometer of Le Boulengé may be mentioned, and the manometric balances of Marcel Deprez based on opposite pressures. An account of them will be found in the "Traité sur la poudre" already quoted (p. 572).

In the same work will also be found a description of the apparatus founded on the dynamic method, such as the experiments made with the ballistic pendulum by Cavalli (1845–1860), and by Neumann (1851), the use of Schulze's chronographs

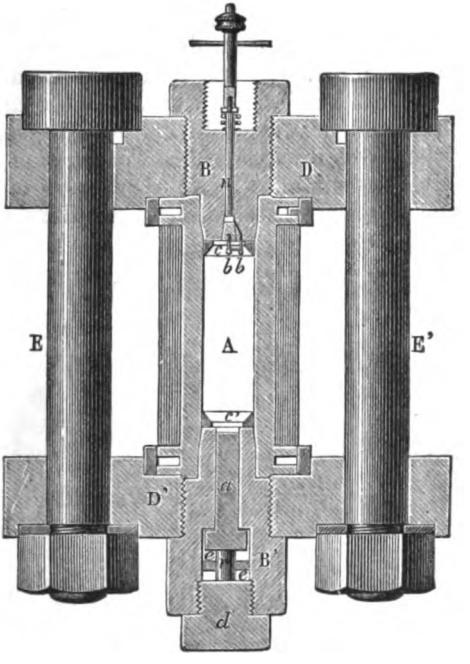

Fig. 1.

(1864), Noble (1872), Noble and Abel (1874), the use of the ballistic pendulum fitted with a metallic plate to measure the effect of impact, by Ph. Hess, and the other similar apparatus invented by that learned Austrian officer (1873–1879), the use of Captain Ricq's recorder (1873), that of the Boulengé monograph, of the accelerometer and accelerograph of Marcel Deprez and Sébert (1873–1878), that of the velocimeter due to Sébert, a learned officer to whom we owe so many ingenious inventions, etc. However noteworthy these instruments may be, their description would carry us too far, and it does not enter into the scope of the present work.

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5. The "crusher" employed in the experiments which the author made in common with M. Vieille, will only be described. In this is measured the crushing of a small cylinder of copper placed between a fixed anvil and the head of a piston with a base of known section which receives the action of the gases.

The eprouvette is of mild steel, 0·022 metres in internal diameter, of a thickness equal to the calibre and of a capacity of 24·3 cms. It is fitted at one end with a plug containing the crushing apparatus which serves for the measurement of the pressures, the other end is closed by a plug carrying the firing arrangement.

In order to avoid all local action at the contact with the metal, the charge is suspended in the centre of the eprouvette in the form of a cylindrical cartridge, of a shape similar to the interior of the chamber. A fine iron wire capable of being brought to a red heat by electricity traverses the cartridge.

Fig. 1 shows the drawing of this eprouvette, frequently employed in the investigations of the Commission des matières explosives. It consists of a cylindrical tube of mild steel, A, strengthened externally, according to Schultz's system, by a

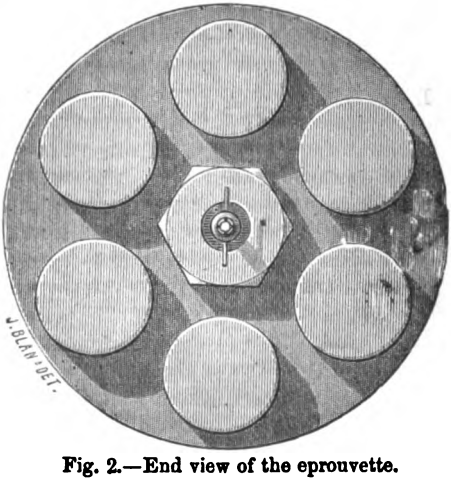

Fig. 2.—End view of the eprouvette.

steel wire 0·8 mm. in diameter wound on the tube at a tension of 35 kilog. The strengthening covering consists of fifteen coils of wire.

The cylinder is closed at both ends by the steel plugs BB′, the joint between the plugs and the tube being formed by annular copper gas checks, *cc′*. The plugs are screwed into two discs of wrought iron DD′, which latter are held together by six bolts EE′ (Fig. 2).

The ignition of the charge is effected by the incandescence of a metallic wire, stretched between two supports, *bb′*, one of

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which is fixed on the plug, and the other on a central metallic rod, n, which traverses the plug, from which it is isolated through the interposition of a thin coating of shellac. The crusher, as is well known, was proposed and applied in 1871 in England by Captain Noble, in his researches on the combustion of powder. It is fitted to the plug, B′, and consists of a piston, a, of tempered steel, easily fitting in a channel following the axis of the plug, and of a cylinder of copper, r, 0·008 metres in diameter and 0·013 metres in height, placed between the piston-head and stopper screwed into the plug.

6. In the method of calibration adopted by the naval artillery, the cylinders are crushed under weights acting without initial velocity, and the reduced heights of the crushed cylinders are measured. From this, by interpolation, is derived a table establishing empirical relations between these heights h, called *remaining heights*, and the corresponding weights, R. Taking π to represent the maximum pressure developed in an experiment, and ω the area of the base of the piston, π is calculated by the ratio $\pi\omega = R$. In order to keep the pressure within the limits of the testing table, it is sufficient to vary the base of the piston.

The results obtained are compared by introducing into the same chamber increasing weights of the explosive substance. The ratio of the weight of the explosive to the internal volume of the eprouvette, is termed the density of charge (see p. 28).

7. The theory of crushing manometers, such as the crusher above described, has been examined in a most thorough manner by Sarrau and Vieille.[1] They first calibrated the apparatus by crushing the cylinder progressively and slowly by very small amounts, until it supported without permanent deformation a given charge. From this was obtained a ratio between the final charge, called the force of calibration (*force de tarage*), θ and the diminution in the height of the cylinder, that is, the corresponding crushing ϵ. K_0 and K being constants independent of the explosive, θ varying from 1000 kgms. to 3500 kgms., we have

$$(1) \quad \theta = K_0 + K\epsilon : K_0 = 541 : K = 535,$$

the units being the millimetre and kilogramme.

This relation being established, how can the resulting indication be applied to experiments? Two limiting cases present themselves:

(a) The development of the pressure is slow enough, and the mass of the crushing piston small enough, to permit of the forces of inertia being neglected; in this case there is practically equilibrium between the pressure developed by the explosion and the resistance of the cylinder. The maximum pressure is

[1] "Comptes rendus des séances de l'Académie des Sciences," pp. 26, 130, et 180. 1882.

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then equal to the force of calibration corresponding to the crushing observed. It is given by formula (1).

(*b*) The development of the pressure is so rapid that the displacement of the piston taking place during the development of the maximum pressure may be disregarded, the piston having, besides, a sufficient mass; in this case the movement of the piston may be regarded as effected under constant pressure from the start, and throughout the whole of its duration. The calculation shows that the value of this pressure is equal to a force of calibration corresponding to half the crushing.

$$(2)\quad \theta = K_0 + \frac{K\epsilon}{2}.$$

8. In practice, and for a given explosive, it has to be ascertained whether the instrument works at one or other of these limits, then to estimate the maximum pressure applicable to the intermediate cases. Hence, it is necessary to register the duration of the crushing, as well as the law of the movement of the piston, and to compare the latter with the results given by calculation for the movement of the piston crushing the cylinder under the action of a force which would be a function of the time. Theory shows that the phenomenon is ruled by the ratio existing between the effective duration, τ, of the crushing taking place under variable pressure and the duration, τ_0, of this crushing caused by a constant force acting on the piston without initial velocity.

However, it is preferable to substitute for a correction which is always somewhat doubtful, data obtained under experimental conditions near one or other limit. We will give some results.

The authors have found for gunpowder, that the crushing remains the same when $\frac{\tau}{\tau_0}$ varies from 4·8 to 251, variations which depend upon the degree of aggregation of the powder (dust, grain, cake, compressed blocks). We are, therefore, always in the neighbourhood of the first limit; that is to say, formula (1) is applicable in all cases.

The maximum pressure of powder gases at the density of charge 0·70 has thus been found equal to 3574 kgms. per sq. cm. Powdered potassium picrate, on the contrary, was so rapidly decomposed that no appreciable value could be observed for τ (expressed in ten-thousandths of a second). The maximum pressure was found equal to 1985 kgms. under a density of charge 0·30. The same salt in compressed blocks gave a more appreciable duration of combustion; or 0·0005 secs. to 0·0006 secs. and a less amount of crushing. It is, therefore, the other limit which must be applied, and this has been experimentally verified.

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With powdered gun-cotton (density of charge 0·20), τ is also inappreciable, and the maximum pressure equal to 1985 kgms., the weight of the piston having varied from 727 grms. to 42·7 grms. Dynamite (density of charge 0·30) is decomposed slower than gun-cotton, but quicker than black powder; the detonation being of course produced by the aid of fulminate. It therefore supplies an intermediate case, in which the discussion of the measurements is more delicate. By employing pistons of medium weight, and even light pistons, it is very difficult to attain the lower limit (1), at least with a certainty comparable to that of the experiments relative to the preceding substances. On the other hand, towards the opposite limit (2), the ratio $\frac{\tau}{\tau_0}$ may be neglected by giving the piston a mass of 4 kgms.; the crushing was then nearly double that obtained with pistons weighing 3·8 grms. and 6·9 grms. Hence, it can be seen that the two limiting cases have been realized with dynamite, as also the intermediate cases, by modifying the mass of the piston.

The maximum pressure for a piston of 4 kgms. has been found equal to 2413 kgms. per sq. cm. for the density of charge 0·30. With a piston of mean weight, that is weighing only 59·7 grms., the density of charge still being 0·30, dynamite and picrate give the same crushing; however, the maximum pressures are very different.

What characterises the experiments made with dynamite is, that the calculation made for very light pistons from formula (1), and for very heavy pistons from formula (2), should give, and in fact does give, the same figure for the value of the pressure exerted.

It is clear from the above with what precaution the crushers must be employed to measure the maximum pressures of explosives. The study of these pressures should be made by the new method of Sarrau and Vieille.

9. It should here be remarked that the measurements thus obtained correspond only to a certain mean of pressures, a mean which is capable of being considerably exceeded at certain points. In reality, the gases suddenly developed by the chemical reaction represent real whirlwinds in which there exist jets of matter under very different states of compression, and an interior fluctuation. This is shown by the mechanical effects produced by these gases on solid substances, and especially on metals, which are hollowed and furrowed in places as if they had received the impress of an extremely hard solid body.

The measurement of initial pressures in cannons likewise manifests local irregularities and differences, sometimes enormous, between the pressures observed at the same instant at

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various points of the chamber where the combustion of the powder takes place.

The pressure, then, is not uniform, and it may vary in an almost discontinuous manner as well as the movement at first communicated to the projectile.

Second Section.—Calculations.

In order to give a better idea of the value of the results calculated by the ordinary laws of gases, such as there are known at about the atmospheric pressure and the ordinary temperature, we will give the experimental measurements made on certain explosive bodies, which do not give dissociable products (at least to an appreciable extent), and which give by their decomposition elementary bodies or gases formed without condensation: for example, carbonic oxide, of which the specific heat is comparable to that of the simple gases. Such are nitrogen sulphide, decomposable into sulphur and nitrogen, and mercury fulminate, decomposable into mercury and carbonic oxide. They will supply us with types for calculations of this kind.

1. Take, for instance, 10 grms. of mercury fulminate detonating in a capacity of 50 cms. (density of charge 0·2). The heat liberated amounts to 114,500 cal. for the reaction,

$$C_2HgN_2O_2 = 2CO + N_2 + Hg;$$

but the mercury being gaseous, the heat of vaporisation must be deducted in calculating the pressure, say 15,400; which reduces the heat available for increasing the pressure to 99,100 cal.

Taking for the value of the specific heat at constant volume of carbonic oxide as well as for that of nitrogen and mercury, each at its molecular weight, the figure 4·8 (a figure, moreover, which is in accordance with experiment for the two first bodies), and neglecting the deviation which exists between this number and the specific heat of liquid mercury, we find for the temperature produced—

$$\frac{99,100}{4 \times 4{\cdot}8} = 5161°.$$

The volume of the permanent gases (nitrogen and carbonic oxide) given by the reaction and reduced to 0° and 0·760 metres will be 22·32 litres × 3.

At a temperature t it becomes

$$22{\cdot}32 \times 3 \times \left(1 + \frac{t}{273}\right).$$

To this should be added, starting from 360°, and at the pressure 0·760 metres, a volume 22·32 lit. $\left(1 + \frac{t}{273}\right)$ of mercury vapour.

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We will thus definitely obtain at the temperature t, supposed higher than 360°, and at the normal pressure, a volume of gas equal to 89·28 lit. $\left(1 + \frac{t}{273}\right)$.

At 5161° this would make 1776 litres from a weight of fulminate equal to 284 grms. Now, the capacity in which the explosion took place being 50 cms. for 10 grms., would be 1·42 litres for 284 grms. Hence the corresponding pressure would be, by Mariotte's law, $\frac{1776}{1{\cdot}42} = 1251$ atm., or 1293 kgms. per sq. cm. The experiment made with a crusher gave a crushing ϵ of 2·4 mms. Mercury fulminate belonging to the class of explosives for which the duration of the development of the pressure may be neglected (p. 23) compared with the duration of working of the crushing apparatus, formula (2) (p. 24) should be applied, that is, $541 + 535\frac{\epsilon}{2}$. This gives 1183 kgms. per sq. cm. Water between 1293 and 1183 is hardly one-twelfth.

Similarly for the density of charge 0·3 theory deduced from Mariotte's law gives 1939 kgms., and the crusher 1871 kgms.

It should further be noted that the value 1183 leads to the specific pressure 5915 kgms., while the value 1871 gives 6233 kgms. (pressure of unit weight in unit volume); figures which are sufficiently close to each other to allow of the mean being taken—6100 kgms. in round numbers.

2. Take, again, nitrogen sulphide. This body has been exploded in a closed vessel, and it has been found that

$$NS = N + S, \text{ develops } + 32{,}300 \text{ cal.}$$

To calculate the pressure at the moment of explosion the heat absorbed by the vaporization of the sulphur must be deducted. If this transformation took place towards 448°, it would absorb about 2600 cal., and there would remain + 29,700 cal. But this figure is still too high, the temperature of the sulphur being raised during the explosion to a point at which this body resumes its theoretical gaseous density, instead of a triple density which it has at 448°. This new transformation absorbs a considerable quantity of heat, which we will estimate provisionally after the analogy of the polymers at 15,000 or 20,000 cal. for S^4, or 8000 to 10,000 cal. for S^2. We thus arrive at about 24,000 cal., a figure which will be employed in default of fuller knowledge. Let us admit that the sum of the specific heats at constant volume of nitrogen and sulphur be equal to 4·8 at every temperature, and neglect the differences between the theoretical specific heat of sulphur and its real specific heat, in the solid and liquid states, in order to simplify the calculations.

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The temperature of the system developed by the explosion will then be—

$$\frac{21{,}000}{4{\cdot}8} = 4375°.$$

The volume of the permanent gases considered at a sufficiently high temperature and at the normal pressure, being here

$$22{\cdot}32 \text{ lit.} \left(1 + \frac{t}{273}\right),$$

at 4375° will be 380 litres, this volume being yielded by 46 grms. of nitrogen sulphide.

Such a weight exploding in a capacity of 230 cms. would develop by Mariotte's law a pressure equal to 1652 atm., or 1707 kgms. per sq. cm.

Now, the trial made with a crusher at a density of charge 0·20, and calculated by the old process, gave 1703 kgms. Here the calculated pressure is practically equal to the pressure given by the crusher. But according to the new theory it would be necessary to correct the latter figure, and to take into account the uncertainty of the estimation of the heat of transformation of sulphur.

Hence it will be seen that direct experiments are necessary. However, deviations of quite a different kind might have been expected.

Third Section.—Density of Charge and Specific Pressure.

1. The relation between the number of grammes expressing the weight of the explosive substance and the number of cubic centimetres expressing the capacity in which the explosion takes place is termed *density of charge.* Now, *if bodies susceptible of being completely transformed into gas at the temperature of the explosion be operated upon,* Mariotte's law shows *that the pressure developed should be proportional to the density of charge.* The temperature, moreover, would remain the same in all cases.

2. This relation may be regarded as accurate for very low densities of charge; the ordinary laws of gases being applicable between these limits. But it ceases to be so for medium densities, starting from 0·1 to 0·2, as might be expected, owing to the inaccuracy of Mariotte's and Gay-Lussac's laws for the corresponding pressures.

3. However, strange to say, the relation again tends to exist for high densities of charge, which are the most interesting for us. This approximate coincidence results, doubtless, from some compensation between the variation of the pressures, which is more rapid than Mariotte's law would show, and the variation in the specific heats, which increase with the temperature and pressure

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(see p. 11), instead of remaining constant, as we have assumed in our calculations. The dissociation, moreover, must be *nil*, or reduced to the minimum for such considerable pressures. This phenomenon does not enter into the question for nitrogen sulphide, a compound resolvable into its elements by explosion.

4. However this may be, this relation has been found to be approached by Sarrau and Vieille in their researches on nitroglycerin and gun-cotton, substances furnishing no solid residue, and such, moreover, that the products of their explosion are susceptible of dissociation.

5. The experiments the author has made in common with M. Vieille on nitrogen sulphide, and on mercury fulminate under the conditions where the explosive substance is entirely changed into gas, and, what is most essential into non-dissociated gases, confirm it in a most positive manner. For example, mercury fulminate having been taken with densities of charge equal to 0·20 and 0·30, the results given by the crusher, calculated according to the new estimate of the force of calibration (*forces de tarage*), show for a density of charge equal to unity (1 grm. in 1 cm.) 5915 kgms. according to the first experiment; 6233 according to the second (see pp. 26, 27), figures which are sufficiently near each other for us to admit the verification of the law. Similarly with nitrogen sulphide, for the density of charge 0·30 we have found, from the indication of the crusher calculated in the ordinary way, a pressure of 2441 kgms., which gives 8140 for the density 1. A second experiment made with the density 0·2, which reduced to unity gives 8500 kgms., shows scarcely any deviation.

Lastly, for gun-cotton, Sarrau and Vieille have found at different densities of charge, figures fluctuating near a constant value of about 10,000 kgms., according to their new theory.

6. All these figures verify the approximate proportion between the pressure developed and the density of charge. Some of these have been calculated by means of the indications of the crushers, according to the old method of estimating the forces of calibration, and by simply deducing the pressure from the remaining height of the crushed cylinder. But it is easy to show that the same practical verifications may be arrived at, at least for high pressures, by the new theory of Sarrau and Vieille. Let us first suppose the pressure equal to the force of calibration.

$$\theta = K_0 + K\varepsilon$$

in the case of explosive substances of which the action is not too rapid (p. 23); K_0 and K being constants independent of the explosive substance. Hence it results that for high pressure the pressure tends to become proportional to ε. The indications based on the force of calibration calculated on the old system retain, therefore, their signification in this case, and it is the

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same with the empirical relations which may be deduced from these indications.

Now take an explosive substance of which the action is extremely rapid (p. 24). In this case the pressure is equal to a force of calibration corresponding to the half of the crushing, $K_0 + \frac{K}{2}\epsilon$, the constants retaining the same value as above. Here again, for one and the same substance, the high pressures tend to become proportional to the crushing ϵ; but the indications deduced from the calibration must be reduced by half.

7. Thus the limiting value of the pressure reduced to the unit of density of charge appears to be a constant; let it be called f; then

$$f = \frac{s}{\Delta},$$

s being the pressure observed for a density of charge, Δ. This constant is characteristic for each explosive substance, and may be called *specific pressure*. It corresponds to one of the definitions which has been given of the force of explosive substances, viz. the pressure developed by unit weight of the substance detonating in unit volume.

8. *Maximum Effort.* It should be observed, however, that the specific pressure does not represent the *maximum effort* which an explosive substance can develop. In fact, this effort is that of a substance detonating in a space entirely filled, that is, in a space equal to its own volume. Now the latter only corresponds to the specific pressure for a body of which the absolute density equals unity. It will therefore be less for a body of which the density is less than unity, as in the case of gaseous mixtures and explosive gases, as well as of certain liquids. On the contrary, it will be greater for all solid explosive substances known up to the present.

It may be calculated, and in fact, from the preceding law it is easy to estimate, the effort of a substance detonating in a completely filled space, it being sufficient to multiply the characteristic number of the pressures by the real density of the pure substance. For instance, the density of mercury fulminate being equal to 4·42, this body would develop a pressure of about 27,000 kgms. per sq. cm. by exploding in its own volume: an enormous figure, and higher than that of all known explosives.

9. Up till now, in the calculations of the specific pressure and of the maximum effort, we have supposed that the explosive substance is entirely transformed into gaseous products. But it may happen that a portion of the substance keeps its solid state, which is the case, for instance, with dynamite, a mixture of nitroglycerin and silicious earth. The volume of the latter

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solid matter must then be deducted from that of the capacity in which the explosion occurs.

We can put, more simply,

$$f = s_1\left(\frac{1 - a\Delta}{\Delta}\right),$$

s_1 being the pressure observed (in kgms.), Δ the density of charge (ratio between the number of grms. representing the weight of the substance and the number of cub. cms. representing the capacity), a the volume expressed in cub. cms., of the solid or liquid products resulting from the combustion of 1 grm. of explosive substance, measured at the temperature of the explosion.

Further, putting $\frac{\Delta}{1} = n$; $f = s_1(n - a)$, n here expressing the ratio of the capacity, expressed in cub. cms., to the weight of the substance expressed in grms.

10. The relation thus modified has been verified, at least approximately for dynamite, by Sarrau and Vieille.

It also represents the experiments of Noble and Abel on the explosion of black powder. In fact, by supposing $a = 0{\cdot}68$ and $f = 2193$ kgms., the numbers found by these authorities give for pebble and R.L.G. powders,

Density of charge.	Pressure per sq. cm. Measured.	Calculated.
0·1	231 kgms. ...	235 kgms.
0·2	513 „ ...	508 „
0·3	839 „ ...	828 „
0·4	1220 „ ...	1207 „
0·5	1684 „ ...	1666 „
0·6	2266 „ ...	2230 „
0·7	3006 „ ...	2963 „
0·8	3912 „ ...	3869 „
0·9	5112 „ ...	5127 „
1·0	6569 „ ...	6926 „

At first sight it appears that these latter results tend to exclude the hypothesis of the total vaporisation of the products yielded by the explosion of black powder. However, the easy vaporisation of potassium sulphide at temperatures lower than 1000° tends to encourage the supposition with respect to this body that it assumes the gaseous form at the temperature of the explosion of powder, and the experiments [1] of Bousingault would also permit of our conceiving the gaseous state of potassium sulphate and carbonate. This point, therefore, remains reserved. There is all the more reason for this, as the co-efficient, a, can be

[1] "Annales de Chime et de Physique," 4e série, tom. xii. p. 428.

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explained equally well by the new laws applicable to the calculation of pressures in very highly compressed gases.

Instead of the above formula, the following may be employed:—

$$s_1 = \frac{4030}{n - 0{\cdot}55},$$

which gives somewhat higher results, but which would appear preferable in some respects.[1]

11. In the calculations in Book III., it has been thought useful, notwithstanding the previous reservations, to give the calculation of the theoretical pressure according to the laws of Mariotte and Gay-Lussac. But care has been taken to define the result with reference to the density of charge $\frac{1}{n}$, instead of merely taking the density 1.

This offers the advantage that the figure thus defined has a physical signification for low densities of charge. For high densities its value becomes more and more dubious. However, it can still be employed in a certain number of comparisons, as follows from what has preceded.

12. The permanent pressure will also be given, that is, the pressure exerted by the permanent gases, produced by the explosion in a completely closed and resisting vessel, and reduced to 0°. This pressure will always be calculated for a density of charge $\frac{1}{n}$. In fact, it cannot exceed the tension of liquefaction of the gases experimented upon.

Fourth Section.—"Characteristic Product."

1. Another simpler term of comparison deduced solely from experimental data can be presented in the study of the pressure developed by explosive substances, viz. the product of the reduced volume of the gases, V_0, by the heat liberated, Q, this product being divided by the specific heat, *c*. The latter is calculated by referring it to the weight of matter capable of producing this volume and quantity of heat.

By this means is obtained the expression

$$\frac{V_0 Q}{c},$$

which may be termed the "characteristic product."

2. It is sufficient to divide it by the actual volume, *n* (expressed in cub. cms.), of the capacity in which the unit weight of the explosive substance has been placed, in order to refer it to the density of charge $\frac{1}{n}$:

[1] "Mémorial de l'Artillerie de Marine," tom. x. p. 187.

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$$\frac{V_0 Q}{nc}.$$

3. In the case where there exist along with the gases fixed substances, so that the unit weight of the explosive substance yields a quantity of fixed substance occupying a fraction of a cub. cm., a, it will be necessary to replace $\frac{V_0 Q}{nc}$ by

$$\frac{V_0 Q}{(n - a)c}.$$

4. The expression which has just been defined is almost exactly proportional to the theoretical pressure for any two explosive substances capable of being entirely changed into gas at the temperature of the explosion.

Now, for a given substance, the theoretical pressure is given by the expression

$$W_n = \frac{V_0\left(1 + \frac{Q}{273c}\right)}{n},$$

If the temperatures were reckoned from the absolute zero this expression would become

$$\frac{V_0 Q}{273nc},$$

that is to say, that it would be identical, with the exception of a multiple, with the characteristic product.

For another substance, enclosed in the same capacity, under the same density of charge there will be

$$W'_n = \frac{V'_0\left(1 + \frac{Q'}{273c'}\right)}{n},$$

an expression which would become from the absolute zero

$$\frac{V'_0 Q'}{273nc'}.$$

In reality action takes place at an initial temperature higher than the absolute zero; but it should be noted that if the quotient $\frac{Q}{273c}$ represents a number much greater than unity, the ratio of the theoretical pressures for two given substances, that is

$$\frac{V_0\left(1 + \frac{Q}{273c}\right)}{V'_0\left(1 + \frac{Q'}{273c'}\right)},$$

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will be practically the same as the simpler ratio,

$$\frac{V_0 Q}{V'_0 Q'} \times \frac{c'}{c}.$$

5. In the case where the specific heats are the same, or very nearly so, which is that of powders having a nitrate as base, and a certain number of other explosive substances, this ratio reduces itself to

$$\frac{V_0 Q}{V'_0 Q'}$$

6. In other cases, if it be supposed with some mathematicians that the specific heat of a compound is equal in theory to the sum of those of its elements, the ratio of the specific heats $\frac{c'}{c}$ might be replaced by the ratio $\frac{q'}{q}$ of the number of the atoms, that is, of the elementary units of the compound (each of these units being referred to its atomic weight), or

$$\frac{V_0 Q}{V'_0 Q'} \times \frac{q'}{q}.$$

But this formula is very open to dispute, owing to the inaccuracy of the hypothesis relative to the specific heats (see p. 19). On this point, we will only state that the specific heat of a molecule of potassium sulphate would be according to theory[1] equal to $2{\cdot}4 \times 7 = 16{\cdot}8$, while experiments have given, even near the ordinary temperature, 33·2, that is, the double. It would be easy to give very numerous examples of the same kind, derived from the study of solid and liquid compounds.

7. Owing to these disagreements, it is preferable to take for c and c' their experimental values, and to admit that their ratio remains nearly constant, notwithstanding the doubts which are connected with the application of these values to very high temperatures.

The ratio of the characteristic products

$$\frac{V_0 Q c'}{V'_0 Q' c}$$

therefore only retains a purely empirical meaning, but it offers the advantage of being calculable for the unit weight, from simply experimental data, and without introducing any hypothesis relative to the laws of gases. It furnishes the elements of a first comparison between explosive substances, in the room of a more perfect theory.

[1] 2·4 is the specific heat at constant volume of the simple gases.

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CHAPTER V.

DURATION OF EXPLOSIVE REACTIONS.

§ 1. General Ideas.

1. The chemical transformation in a mass which explodes, arises and is propagated with a certain rapidity, the knowledge of which is of primary importance for theory, as well as practice. In fact, the rapidity with which the gases are liberated depends upon it, and consequently the velocity communicated to projectiles, as also the effects produced in blasting at the expense of the rocks which it is desired to break up, or the obstacles to be removed in military engineering. Now the heat liberated by a given reaction may be almost entirely employed to heat the gases and increase their pressure, if the reaction be very rapid; while it is dissipated to no purpose by radiation and conduction if the reaction be slow.

In the former case the effects may be very various.

When an instantaneous decomposition takes place, a given quantity of explosive substance crushes on the spot the portions of rock with which it is in contact. Its energy is therefore consumed in a work almost useless from the industrial point of view, but which is sometimes desired in military engineering, with a view to hollowing a primary chamber, destined to contain a larger charge of explosive. If the development of the gases be less sudden, though still extremely rapid, the same quantity of explosive may on the other hand dislocate the rock by producing extended fissures in it, and by hurling abruptly aside the nearest portions of rock, which is in general the result aimed at by miners.

This action is transformed in certain cases into a general shaking, which causes the ground to tremble and considerably displaces the centres of gravity of stones and other objects, thus destroying the stability of masonry and fortified works.

Lastly, the same quantity of explosive sometimes reduces its effects to elastic displacements, and an undulating movement

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of the ground, which are propagated to a distance without great local destruction, the pressures developed having been exerted sufficiently slowly to give the rock or wall time to displace itself very slightly "en masse." In this case the explosive substance will have produced scarcely any useful effect.

This question of the duration of reactions playing an essential part in all questions relative to explosive substances, has led the author to bring together here the principal considerations and experiments to which it has given rise, experiments on which he has been engaged for many years.

2. The chemical transformation of the explosive substance has therefore to be defined from the threefold point of view of its origin, its duration, and its propagation.

§ 2. Origin of Reactions.

1. A reaction, once started, continues by itself, being propagated either by simple progressive inflammation, or by almost instantaneous detonation.

2. In all cases relative to the usual explosive substances, to develop the reaction requires preliminary work,[1] a sort of preparation which is represented by the necessity of raising the substance to a certain initial temperature, such as 315° for black powder, 190° for mercury fulminate, etc. Indeed, if it were otherwise, no explosive substance could be prepared beforehand and stored in a magazine.

But to what point are these notions applicable to the cases in which the reaction results from a shock, a sudden pressure, or any mechanical influence?

3. The author is of opinion that every explosive reaction should be attributed to a preliminary heating, which is gradually transmitted, directly or indirectly, raising successively all the parts of the matter to the temperature of decomposition.

Shock pressure, friction, or mechanical effects are only efficacious by causing this preliminary heating, and sometimes propagating it in virtue of the direct or alternative transformations of the energy into heat, and according to the various mechanisms, to which reference will be made in § 6.

4. This being granted, let it be noted that the decomposition of one and the same substance can take place at very unequal temperatures and velocities; a substance slowly decomposable at a certain temperature being able to exist at much higher temperatures, though during a gradually shortening interval.

It is in this way that certain explosive substances are sometimes spontaneously decomposed with great slowness, from the ordinary temperature, and only produce detonations if the temperature be raised intentionally or by accident.

[1] "Essai de Mécanique Chimique," tom. ii. p. 6.

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The author has, moreover, developed the whole of this theory in another place,[1] and recalls it in order to thoroughly fix the ideas.

5. It plays a very important part in the explanation of the mode of formation of the secondary compounds, produced by the explosion of powder, several of these compounds being formed at the very outset, at temperatures which would gradually destroy them if they lasted long enough. But the suddenness of the cooling keeps the compounds, such as formic acid, ammonia, nitric acid, from the destruction which they would quickly undergo if they were maintained in a constant manner at the initial temperature of their formation. In fact, this sudden cooling brings them to the temperature at which they are definitely stable.

§ 3. Sensitiveness of Explosive Substances.

1. This sensitiveness depends both on condition of heating, and on the mode of propagation of the reactions. It varies according to circumstances. One substance is sensitive to the slightest rise in temperature, another to a sudden pressure, another to shock, properly so called, another detonates with the least friction. Thus for example, silver oxalate detonates at about 130°, nitrogen sulphide at about 207°, mercury fulminate at a temperature near this, about 190°, and nevertheless the fulminate is much more sensitive to shock and friction than nitrogen sulphide and silver oxalate. There exist therefore special properties, depending on the individual structure of each substance, particularly for the solids, which favour decomposition under given circumstances. But there also exist general conditions, which it will now be useful to state.

2. The sensitiveness exhibited by the same substance increases with the initial temperature at which the operation is performed, that is, a temperature nearer to that at which the body commences to be spontaneously decomposed, the explanation of this being that the heat liberated by the reaction proper undergoes less loss by radiation, and that it raises to the desired degree a greater weight of the non-decomposed substance.

A portion of the sensitiveness will be rendered still greater if this limit be exceeded, that is, if the conditions prevail under which a slow decomposition may be transformed by the least heating into a rapid decomposition.

A substance taken near and especially above this limit may be said to be in the state of chemical tension.

For example, *celluloid*, a body which does not detonate under the hammer at the ordinary temperature, acquires the property of detonating when heated to about its softening point,

[1] "Essai de Mécanique Chimique," tom. ii. p. 58 and following.

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viz. towards 160° to 180°, a point which is near the temperature of the rapid decomposition of the substance.

3. When two different explosive substances are compared, which are decomposed at the same temperature and with similar rapidity, their *relative sensitiveness to shock and friction*, at a lower temperature, *depends on the quantity of matter over which, from the first instant, the work of the shock or of the friction is distributed;* that is to say, it depends on the cohesion of the substance, which regulates at the point struck the transformation of energy into heat, and consequently, the temperature developed around this point.

4. Cohesion, also, generally intervenes *in the case of direct inflammation; the same quantity of heat* produced by the combustion of the first portions, *being able to raise to the degree of decomposition the temperature of a small quantity of matter*, to which it is exclusively applied, while *if it be distributed over a greater mass* the temperature of the latter will not be raised to the degree requisite for the decomposition to be propagated.

5. The mass heated remaining the same, and the substances being different, *the sensitiveness depends on the initial temperature at which decomposition commences.* This temperature being considerably lower, for example, for potassium chlorate than for the nitrate, the chlorate powder will be more sensitive in this respect.

6. *The sensitiveness depends* furthermore *on the quantity of heat liberated by decomposition;* that is to say, that the sensitiveness will be greater, all things else being equal, if the reaction liberates more heat.

7. *The same quantity of heat will produce different effects on the same weight of matter according to the specific heat of the latter.* For instance, potassium chlorate, the specific heat of which is 0·209, substituted for an equal weight of potassium nitrate, of which the specific heat is 0·239, in the composition of an explosive mixture should give, and in fact does give, a more sensitive powder than the nitrate.

This condition contributes, with the lower temperature of decomposition and the absence of cohesion, to render the chlorate powders eminently dangerous.

§ 4. Molecular Rapidity of the Reactions.

First Section.—General Phenomena.

1. The rapidity of a reaction must be regarded in a different manner according as it is the question of a homogeneous system, and especially of a gaseous system, submitted to identical conditions of temperature and pressure in all its parts, or if the system be submitted at one point to a rise in temperature or

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to a shock capable of producing an explosion which is then gradually propagated.

Let us first examine the former case. We shall distinguish the *molecular rapidity of the reactions*, which is defined by the quantity of matter transformed at a fixed temperature and constant pressure, under invariable conditions, *and the rapidity of propagation of reactions.*

For greater clearness the phenomena will be treated in a general manner in the first section, then the molecular rapidity of reactions in a homogeneous system, submitted to uniform conditions and contained in an enclosure to which it cannot yield, and from which it cannot borrow heat, will be specially studied (second section). Lastly, a system also homogeneous, but which can lose heat, will be examined (third section).

2. Suppose, first, a certain body, or a certain mixture, capable of undergoing a chemical transformation. When the whole mass is placed under the same conditions of temperature, pressure, or of vibratory movement, etc., it seems as if the reaction must be instantaneously developed in all the parts at the same time; the sudden explosions of nitrogen chloride and of nitroglycerin would seem favourable to this idea at first sight. However, a closer observation proves that molecular reactions generally require a certain time for their accomplishment, even when they liberate heat. Such is, for instance, the decomposition of formic acid into hydrogen and carbonic acid, which can be easily followed experimentally owing to the slowness with which this decomposition is effected. Carried out in a closed vessel and maintained at the fixed temperature of 260°, it requires many hours. Nevertheless this reaction liberates 5800 cal. per equivalent of formic acid, viz. 126 cal. per gramme.[1]

3. The following are further examples of reactions liberating a large quantity of heat, without, however, being instantaneous.

Thus, acetylene, changed into benzene towards a dull red heat by a slow reaction, liberates at the same volume half as much heat again as a detonating mixture formed of oxygen and hydrogen in the proportions of water, viz. 85,500 cal. for 33·6 litres of acetylene (reduced to 0° and 0·760), instead of 59,000 cal., produced by the formation of gaseous water by means of the same volume of electrolytic gas.

It is about four times as much as the heat liberated by a chlorate powder, weight for weight, viz. 2192 cal. per 1 grm. of transformed acetylene, instead of 590·6 cal. for 1 grm. of potassium chlorate powder.

Cyanogen liberates three times as much (1435 cal. per 1 grm.) as the same weight of chlorate powder, and this number is

[1] "Essai de Mécanique Chimique," tom. ii. p. 17, and especially p. 58 and following.

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double that of the heat liberated by an explosive mixture formed of electrolytic gas at the same volume, viz. 33·6 litres, or 112,000 cal. instead of 59,000, when the cyanogen is decomposed into free carbon and nitrogen by the electric spark. Nevertheless, even though the carbon immediately commences to be precipitated, the cyanogen does not detonate under the influence of the spark, nor even of the voltaic arc, which is a proof of the slowness of the reaction thus caused.

Under other conditions, however, the cyanogen and acetylene can be decomposed with detonation into their elements, but it is neither by simple heating nor by the action of the electric arc or spark (see p. 67).

Instances might be multiplied of these facts[1] which comprise the explosive bodies, properly so called, when maintained at a temperature slightly less than that which determines the explosion. Silver oxalate, for instance, is slowly decomposed at 100°, while it detonates sharply at a slightly higher temperature.

4. In a word, every molecular reaction effected by simple heating at a constant temperature in a homogeneous body and submitted to conditions which appear identical for all its parts, has a characteristic coefficient relative to the duration. This coefficient depends on the temperature, the pressure, and the relative proportions; it plays a very important part in the study of the unequally destructive properties of explosive compounds.

This will be exemplified by a few applications.

5. The longer or shorter duration of a reaction does not change the quantity of heat liberated by the total transformation of a given weight of explosive matter. But if the gases formed gradually expand, for instance, as in a cannon, owing to the change of capacity, increased by the flight of the projectile, or owing to cooling due to contact with the walls of the vessel; under these circumstances the initial pressures will be less the longer the transformation of a given weight of matter lasts.

On the contrary, when a very rapid transformation of the whole mass in a closed vessel, allows the initial pressures to attain the immensity of their theoretical limits, or to approach it, it is difficult to construct vessels strong enough to contain the gases of explosion.

6. This explains the influence of resisting envelopes and of tamping, an influence which is especially apparent with slow powders, but which is also observed with rapid powders, particularly in detonators.

At the moment of the explosion the pressure at first developed around the ignited point tends to diminish, owing to the expansion of the gases, and in proportion as the products are distributed throughout a more considerable space. If the gases

[1] "Annales de Chimie et de Physique," 4ᵉ série, tom. xviii. p. 142.

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retained the whole of their heat the pressure after some instants would depend solely on the extent of the space. The pressure would be greater the more limited the space; the maximum pressure corresponding to the explosion of the substance in its own volume, and the molecular rapidity of the reaction exerting no influence. But this is an extreme limit, owing to the losses of heat which the products of the explosion continually undergo by contact, conduction, and radiation; hence results a cooling, which lowers the temperature, and therefore the pressure, as well as the rapidity of the chemical reaction. The initial pressure tends to approach this limit, the more rapid the powder, the smaller the capacity enclosing the powder, and the more resisting the walls of this capacity, which enables them to hold the compressed gases during a longer period.

7. The same will happen, not only when an explosive body is placed in a fixed and resisting capacity, but also if it be placed in a thin envelope, or under a stratum of water, or even in the open air. In fact, when the duration of reaction decreases beyond measure, the gases liberated develop pressures which increase with an extreme rapidity, so rapidly, indeed, that the surrounding bodies, solid, liquid, or even gaseous, have not time to put themselves in motion in order to yield gradually to these pressures; these bodies, therefore, offer to the expansion of the gases resistances comparable to those of a fixed wall.

It is known that a film of water on the surface of nitrogen chloride is sufficient to give rise to such effects. A drop of this substance placed in a watch-glass may detonate without breaking it, while if it be covered with a little water the glass is broken. By operating on a slightly larger mass, even the plank upon which the vessel is placed may be pierced under these conditions.

The same result may sometimes be attained by increasing the mass of the explosive substance; the gases first ignited not having time to dissipate, are then acting as tamping. This effect becomes greater and greater, as the temperature of the substance, and therefore the rapidity of the reaction, increases.

It is in this way that compressed dynamite and gun-cotton, substances capable of being inflamed without danger by the aid of an ignited body when operated upon in small quantities, have sometimes caused terrible explosions, owing to the general inflammation of a considerable mass.

To sum up, the nearer the duration of the reaction approaches being instantaneous, the nearer the initial pressure, even in an open vessel, approaches the theoretical pressure, the latter being calculated for the case of a decomposition effected in a constant capacity entirely filled by the explosive substance. It is thus that the extraordinary destructive effects produced by mercury fulminate, nitroglycerin, or compressed gun-cotton can be appreciated.

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We shall now analyse the phenomena in a more precise manner.

Second Section.—A homogeneous system submitted to uniform conditions and contained in an enclosure to which it cannot yield, and from which it cannot take any heat.

Let it be a homogeneous system capable of disengaging heat by chemical transformation.

The case will first be examined where *this system is submitted to uniform conditions in all its parts, and contained in an enclosure to which it cannot yield, and from which it cannot take any heat.* Under these theoretical conditions, the mass of the matter is of no importance.

1. The *molecular rapidity of reactions in a homogeneous system*, everything else being equal, *increases with the temperature.*[1] Indeed, it increases according to a very rapid law, as is proved by the author's experiments on ethers,[2] the rapidity being then represented by an exponential function of the temperature, a function of which the numerical value, in the formation of acetic ether, is 22,000 times greater near 200° than near 7°.

2. *The temperature of the system increases, at least up to a certain limit, by the very effect of the reaction.*

The temperature of the system increases, at first incessantly, and does so up to a limit defined by the figure obtained by dividing the heat liberated by unit weight by the specific heat of the system.

Further, the rapidity with which the system tends towards this limit goes on increasing according as the rise in temperature produced by the reaction itself is more considerable.

In a gaseous system contained in a fixed enclosure the acceleration will become even greater, at least at the commencement, and this owing to the influence of pressure, which necessarily increases by the fact of the rise in temperature. In short, the author has established that, everything else being equal, and while operating at a fixed temperature, the reactions are affected more rapidly in liquid than in gaseous media. In gaseous media, in particular, he has recognised that the reactions are the more rapid the greater the pressure.[3]

3. *The molecular rapidity of the reactions in a homogeneous system, increases with the condensation of the substances*, or more simply, *the rapidity of the reactions increases with the pressure in gaseous systems.*[4]

Thus, in an enclosure supposed impermeable to heat the

[1] "Essai de Mécanique Chimique," tom. ii. p. 64.
[2] Ibid., p. 93.
[3] Ibid., p. 94.
[4] In solid or liquid systems, on the contrary, the pressure exerts little influence according to the author's experiments, which is conceivable because it hardly modifies the state of condensation of the substances.

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elementary rapidity of the reactions will go on incessantly increasing, for the twofold reason that the temperature is continually rising and that the pressure of the gases is continually increasing.

However, the influence of pressure will be more sensible at the beginning than at the end of the experiment, seeing that the non-combined part diminishes more and more, and that there arrives a moment when the tension proper of this part, considered independently of the rest, ceases to go on increasing in consequence of the heating.

4. *The molecular rapidity of reactions in a homogeneous system depends on the relative proportions of the components.*

When operating at *constant temperature*, the combination is greatly accelerated by the presence of an excess of either of the components.

At constant temperature, the action is, on the contrary, checked by the presence of an inert substance which acts by diminishing the state of condensation of the substance.

At variable temperature the reactions are *à fortiori* retarded by the presence of an inert body, such as the nitrogen of the air, or the silica of ordinary dynamite, this inert body absorbing the heat and lowering the temperature of the system without exerting any influence tending to accelerate it by its presence.

At variable temperature the reaction is generally slower in presence of an excess of one of the components than if equal equivalents be used, the necessity of heating this excess more than compensating its accelerating influence.

It is clear that if the proportion of the inert matter be such that the temperature of the system cannot be raised to the degree necessary for the combination to be continued of itself the reaction will cease to be explosive, and even to propagate itself.

It is in this way that the character of explosive substances may be changed by mixture with an inert body. The following are some characteristic facts.

Dynamite of 75 per cent. is less shattering than pure nitroglycerin. However, such dynamite cannot be employed in charging shells, as the latter would explode in the bore of the cannon, under the influence of the initial shock of the powder. Dynamite of 50 or 60 per cent. can, on the contrary, be employed in hollow projectiles, which may be fired from cannons without danger.

This is not all. With dynamite of 60 per cent. the projectile can explode at the point of arrival, even without a special fuse, if it be arrested by a very resisting body, such as an armour plate, the rise of temperature which results from the transformation of the energy into heat, produced by the sudden stoppage, being sufficient to cause the explosion. But if the

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charge of nitroglycerin be lowered to 30 or 40 per cent. the shell charged with such dynamite will require the employment of a percussion fuse in order to explode, as in the case of black powder. It is true that such dynamite scarcely offers any advantage over ordinary powder.

Another essential point is that not only the molecular rapidity is diminished under these conditions, but also the rapidity of inflammation and the rapidity of combustion of an explosive substance are also extremely retarded when it is mixed with an inert body in proportions approaching those which correspond to the limits of inflammability. Consequently, towards these limits inflammation becomes uncertain, combustion is badly propagated, and the explosive character of the phenomenon ceases to be manifest.

Third Section.—A homogeneous system submitted to uniform conditions but capable of losing heat.

1. These general relations being established for a system where all the heat which it liberates is employed to raise the temperature, we come to the real case, that *in which the system still supposed homogeneous and submitted to uniform conditions at the outset yields a portion of its heat to the surrounding bodies by radiation or conduction.* The mass of the substances employed, which does not come into question in principle in the first case, here plays an essential part.

In short, whenever the rapidity of the reactions is not great, a part of the heat produced will be gradually dissipated, and the elevation of temperature will soon attain a certain limit. This limit will be that at which the loss of heat produced by the external actions is equal to the gain due to the internal reactions of the system, the reaction will then take place with a certain rapidity constant or nearly so, without however becoming explosive.

This is the case of a substance fusing under ordinary conditions, and it is also the case, generally in a marked degree of slowness, of a small quantity of an explosive substance which is spontaneously decomposed.

But if the mass operated upon be increased, supposing it contained in a fixed capacity, the quantity of heat lost by radiation or conduction at a given temperature of the system will be less; the total quantity of heat retained in the interior at the end of a given time will therefore be increased. Thus the temperature of such a system must be higher whether it tend towards a new limit superior to the preceding or whether its increase becomes more and more rapid and finally explosive, owing to the correlative increase in the pressures.

This same correlative accelerating of the pressures and of the rapidity of the reactions plays an important part in the inter-

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pretation of the effects of tamping, as has been said before (pp. 40, 41).

It is, further, in this way that every fusing substance may be transformed into a detonating substance, when the mass of it contained in a given capacity is increased, of course without any change being made either in the orifices or the form of the capacity.

The difference between the various modes of decomposition of an explosive substance, according as its mass is more or less considerable, deserve particular attention, for it is continually occurring in practice.

2. This is noticeable even when there is an escape for the gases of the explosion, provided the explosive mass be large enough. It is thus that the decomposition of a fusing substance, taken at constant weight, and contained within a given capacity, may change into explosion, when the orifice of this capacity is contracted in such a manner that the inward pressure and temperature may increase beyond a certain limit.

3. The same remark applies to spontaneous decomposition of great masses of matter. Slow at first at the ordinary temperature, they quicken under the influence of that very increase in temperature to which they themselves give rise. It may also happen that this rise in temperature changes the character of the decomposition by causing a fresh reaction after the initial one, throwing off more heat. The rise in the temperature of the mass hence still further increases, even to the extent of producing a tumultuous reaction, and a general explosion.

4. These facts, often observed in laboratories, have been quoted to account for the spontaneous explosions of gun-cotton and nitroglycerin, and their tendency is to cause us to regard as especially dangerous any explosive substance in which the process of decomposition has commenced.

5. These considerations demonstrate the cause of general explosions, not only of explosive substances contained in very solid vessels, but even in vessels whose resistance is very slight, such as wooden cases or thin metallic envelopes, and again of explosions of substances piled up in the open air when the accumulation of these substances permit of a rise in the temperature and of a gradual acceleration in the reaction (see p. 41).

6. General explosions may also occur with substances divided into very small quantities, if these small quantities are sufficiently close to one another to constitute a large mass in the aggregate, and if the mechanical effects admit of accumulation and to produce a common result.

The precautions, therefore, both for storage and use, should be taken just as though all the individual portions of the explosive substance were collected into one single mass. Herein lie the

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consequences which theory has pointed to as possible, and the accidental realisation of which has been proved by terrible catastrophes.

Thus, for instance, the experiments made by the Birmingham Chamber of Commerce on the transport and storage of amorces have shown that capsules each containing 0·015 grms. of fulminate, do not explode *en masse* either under the influence of a shock, or when crushed by the wheels of a locomotive, or when placed in an incandescent muffle, or in the centre of a burning furnace.

Yet this is not so if the charge of fulminate contained in the capsules be considerably increased. The feeling of security created by these first experiments no longer exists even in England, in consequence of the explosion of a vessel loaded with amorces in the Thames.

Experience has in fact shown that the explosion of one single strong fulminating capsule is sufficient to cause the explosion of all the capsules placed in the same case. If the case itself explodes, all the adjoining cases will also explode.

It is on account of analogous phenomena that the small fulminating caps (amorces), used as children's playthings, have only too often given rise to serious accidents.

At Vanves, near Paris, a child was amusing itself by letting off one of these amorces between the blades of a pair of scissors, when two packets of six hundred amorces that were lying on the table exploded at the same moment. The child was killed, the chair shattered, and the flooring staved in.

The explosion which occurred in Paris, in the Rue Beranger, on May 14, 1878, may also be mentioned, in a store containing amorces intended for children's toys. These amorces were composed as follows:—One kind, called single, of a mixture of potassium chlorate (12 parts), amorphous phosphorus (6 parts), lead oxide (12 parts), and resin (1 part); the others, called double, consisted of a mixture of potassium chlorate (9 parts), amorphous phosphorus (1 part), antimony sulphide (1 part), flowers of sulphur (0·25 part), and nitre (0·25 part). The latter, more sensitive to friction, averaged 0·01 grm. in weight. From six to eight millions of these amorces pasted on paper slips, in lots of five each, were piled up in the warehouse in boxes. A few of these having become ignited by an accident, the origin of which was never clearly ascertained, caused the whole to explode. One building suddenly gave way, the façade being blown out, and the stonework hurled some distance. One stone, measuring a cubic metre, was thrown to a distance of fifty-two metres. A great part of the adjoining building was also destroyed, fourteen persons were killed on the spot, and sixteen received injuries.

These terrible effects are explained when we consider that

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the weight of the entire explosive matter contained in the amorces amounted to about 64 kgms., and that its force, owing to the composition of this matter, was equal to a force of 226 kgms. of black powder.[1]

It is essential, that persons having explosive substances under their charge should never lose sight of the conviction that, from the facts and general truths which have just been stated, preventive measures should always be prescribed on the hypothesis of a total explosion.

§ 5. Rapidity with which Reactions are Propagated.

1. Let us now examine the case of a *homogeneous system*, but *subject to different conditions in its various parts*, such as those resulting from ignition at one point, or from a local shock, conditions to which some of the facts quoted in the preceding paragraph may be ascribed.

For propagating the transformation in a mass which explodes, and is not subject to the same conditions in all its parts, the physical conditions of temperature, pressure, etc., which have incited the phenomenon at one point must reproduce themselves successively from layer to layer throughout every part of the whole mass.

On this head attention may be called to the numerous experiments made by artillerymen, as to the rapidity of the combustion of ordinary powder, and as to that of gun-cotton; the rapidity varying according to the physical construction and chemical composition of the powders. We will firstly sum up these results, as well as those observed with mixtures of gaseous explosives, that is to say, the observations relating to the rapidity of combustion of mixtures of oxygen and hydrogen, or of carbonic oxide, or of hydrocarbon gases.

We shall then speak of the new and unexpected results furnished by the study of gun-cotton and nitroglycerin; describe the new conception of the employment of caps, and the hitherto unknown distinction between the simple ignition and the genuine explosion of explosive matters will be discussed; a distinction which the author's recent experiments led him to extend to gaseous mixtures themselves. Then it will be attempted to apply these differences to theoretical conceptions. Thus we shall be led on to the notion of the explosive wave, which will form the subject of a special chapter.

2. According to Piobert,[2] the rapidity of the combustion of powder in the open air, observed on vertically placed prisms of known length, the lateral surfaces of which were greased for the

[1] These facts have been taken from the report presented by the Committee of Inquiry.

[2] Piobert, "Traité d'Artillerie," partie théorique.

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purpose of ensuring the regularity of the phenomenon, has been found to be between 10 and 13 mms. per second for service powder. It varies, moreover, in an inverse ratio to the apparent density of the powder, in which the fire propagates itself in successive layers.

3. The velocity of combustion in this sense, that is to say, the velocity with which the reaction is transmitted into the interior of a single explosive mass, should not be confounded with the velocity of inflammation, that is, with the time necessary for the propagation of the same reaction in a whole formed out of a series of small masses or grains placed side by side. In order to characterise the difference between these two velocities, we shall give the experiments made by Piobert with hollow iron semi-cylinders of various lengths. The velocity of inflammation, measured in the open air, varies in the old service powders from 1·5 metre to 3·4 metres per second; in tubes closed at one end, from 0·30 metre to 1·5 metre, according as the grain is 0·2 mm. or 2·5 mms. in diameter. The increase is in proportion to the size of the grain. These figures are very different from those given above for the velocity of combustion in a single mass.

4. The combustion velocity of powder depends on the pressure of air or of the surrounding gases.

At the end of the seventeenth century, Boyle made some experiments on the combustion of powder in a vacuum, and observed that, under these circumstances, the grains of powder projected on a red-hot iron fused with detonating. If we try a certain number of grains at the same time, explosion results; doubtless because the conditions of local pressure are changed round each grain which deflagrates.

Huyghens repeated the same experiment by igniting powder by means of a lens which concentrated the solar rays.

If the heating is progressive, as would be obtained by the radiation from a lighted coal, the sulphur may either be sublimed, thus destroying the homogeneity of the compound, or the powder can be fused according to Hawksbee (1702).

These experiments have been often tried with various modifications, such as the employment of a platinum wire brought to red heat by electricity, for the purpose of igniting the powder in a vacuum (Abel). Bianchi has thus observed that gun-cotton slowly decomposes in a vacuum before exploding, and this result has since been extended to nitroglycerin by Heeren and Abel.

Mercury fulminate on the other hand explodes in a vacuum when placed in contact with a brass wire heated to redness; but the explosion does not propagate itself to grains which are not contiguous, as it would do under atmospheric pressure.

5. Not only does a vacuum prevent the explosion of the powder

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but every diminution in pressure retards it. In 1855, Mitchell observed that fuses burn slower on high mountains; some very exact experiments were made in this respect by Frankland in 1861 in his own laboratory, and afterwards by De Saint-Robert in the Alps. Under pressures varying between 0·722 metre and 0·405 metre, that is to say, below atmospheric pressure, the velocity of the combustion of powder would be practically represented, according to De Saint-Robert, by such a formula as the following:

$$V = Ap^{\frac{2}{3}},$$

A being a constant, and p expressing the pressure.

These effects are to be attributed to the greater or less velocity with which the heated gases escape before having had time to heat the adjacent portions of the solid matter. This is equivalent to saying that pressure lessens the number of gaseous particles brought up to a high temperature which at every moment come in contact with the solid particles not yet ignited and share with them their energy, so as to place themselves in equilibrium of temperature.

Whatever the pressure, if it operates under a constant volume, the initial temperature of these particles remains practically the same; at least, so long as the chemical reaction is not modified. But if operating under a constant pressure, the case will be otherwise, the temperature being lowered by the expansion of the gases.

6. On the other hand, the combustion velocity of powder increases with great rapidity, once we obtain the considerable pressures which are produced in cannons and guns. Thus, for instance, Captain Castan estimated the combustion velocity of powder, in the interior of large bore cannons, at 0·32 metre per second, instead of about 0·1 metre in the open air.

7. The combustion velocity of other explosive substances has not formed the object of such numerous experiments as that of black powder; moreover, it gives rise to fresh observations and to a theory of an entirely different order, as will presently be stated.

Piobert estimated the combustion velocity of non-compressed gun-cotton at eight times more than that of service powder; which estimate was applied to a progressive combustion effected without detonation.

8. These researches were extended to explosive gaseous mixtures. In 1867, Bunsen[1] estimated the velocity of combustion for electrolytic gas (hydrogen and oxygen) at 34 metres per second, and at only one metre per second for the mixture of carbonic oxide and oxygen in equivalent proportions, these mixtures being taken under atmospheric pressure. He deter-

[1] "Annales de Chimie et de Physique," 4ᵉ série, tom. xiv. p. 449.

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mined its rate of flow through a narrow orifice, ignited the jet and endeavoured to discover what was the minimum rate of flow at which the flame would remain stationary at the orifice without going back into the interior. Mallard[1] made several experiments on various mixtures of air and of marsh gas, or of coal gas; he found that the velocity of combustion defined as above rapidly diminishes in proportion as the ratio of the gases which do not contribute to the combustion is increased, the maximum speed being 0·560 metre per second in the case of a mixture of eight parts by volume of air and one part of marsh gas. If a mixture contain twelve parts of air and one part of marsh gas it will descend to 0·04 metre. With coal gas and air the maximum velocity obtained has been almost double. Mallard and Le Chatelier have recently returned to this question by other processes which have given them very varied results according to the mode of combustion. This will be referred to later on, and the existence of detonating velocities for the same gaseous mixtures reaching almost up to 3000 metres per second, and the causes of these differences will be shown.

9. The study of new explosive substances has in fact led to a fuller knowledge of the mode of propagation of chemical reaction in the interior of a mass in combustion; and it has radically modified the ideas which prevailed on this question. At one time, when black powder was the only known explosive, the only point studied was how to ignite it, the effects of consecutive explosion not appearing to depend on the process of ignition. But nitroglycerin and gun-cotton have evinced a singular diversity in this respect.

10. To form a correct conception of them, mention must first be made of the phenomena of shock and of other analogous causes capable of producing deflagration.

Shock could hardly of itself affect the decomposition of a substance which absorbs heat, unless recourse be had to colossal masses animated by enormous energy and concentrating all their action on a very small quantity of matter, which is very difficult to effect. For instance, the energy of a weight of 1630 kgms. falling from a height of 1 metre, would be necessary in order to decompose 1 grm. of water, assuming that by any artifice the totality of this energy could be transmitted to a gramme of water.

On the other hand, if the decomposition of the substance disengages heat, we can conceive that a limited energy would suffice to provoke it, provided it were applied in its entirety to a very small quantity of matter whose temperature it raised to the desired degree for determining reaction.

Thus a few heavy strokes of a hammer on potassium chlorate

[1] "Annales de Mines," tom. viii. 3e livraison. 1871.

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wrapped in a sheet of platinum and placed on an anvil, will be sufficient to give rise to the formation of very sensible traces of potassium chloride, whereas under similar conditions potassium sulphate gives no indication whatever of decomposition. But the decomposition of potassium sulphate into potassium sulphide and oxygen absorbs heat, whereas the decomposition of potassium chlorate into potassium chloride disengages heat (11,000 cal. for $KClO_3$).

11. This condition, however, is not sufficient for shock to produce a detonation. It is further necessary that the energy developed by the decomposition of the first portions should be able to communicate itself to the neighbouring parts, so as to determine step by step the decomposition of the whole mass. The most favourable condition is evidently that one in which the particles of the explosive substance are in movement and animated by an energy of such a nature that their sudden stoppage would transform this force into heat in the interior of the substance itself. The substance is thus heated in a uniform and sudden manner; if the proper temperature be attained, the explosion occurs immediately. Such conditions may be realized on the sudden stoppage of a bomb-shell charged with dynamite which meets with a resisting surface (see p. 43). In an opposite sense it may be noted that the shock of a hammer which is hardly sufficient to produce on some isolated points the desired conditions with pure potassium chlorate is, on the contrary, very efficacious with nitroglycerin. Even the fall of a weight of 4·7 kgms. from a height of 0·25 metre on to a drop of nitroglycerin covering a surface of 2 sq. cms. is sufficient to cause the explosion of this substance.[1] On the other hand, nitroglycerin mixed with a silicious earth constitutes dynamite, a substance which is very slightly susceptible to shock, because the porous and cellular structure of the silica militates against the immediate and local communication of energy to a very small portion of nitroglycerin when regarded apart from the rest.

Further, the explosion of black powder causes nitroglycerin to explode, whereas it does not produce the explosion of dynamite, at least in the open air and with weak charges.

But this inertness disappears under the influence of certain particularly violent shocks, such as that of mercury fulminate. Again, the explosion of nitroglycerin is very different, according as it is pure or mixed with another body or is operated on by a simple shock, by contact with a body in weak ignition, or in active ignition, or, again, by the aid of an ordinary fuse; or, finally, by the contact of a strong priming of mercury fulminate.

[1] Ch. Girard, Millot et Vogt ("Comptes rendus des séances de l'Académie des Sciences," tom. lxxi. p. 691).

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§ 6. Multiplicity of the Modes of Combustion.

1. According to the method employed for ignition, dynamite may be quietly decomposed without any flame; or it may burn briskly; or, again, give rise to an explosion properly so called, either moderate, or capable of dislocating rocks, or even of locally crushing them and of producing the most violent effects.

2. The substances which determine these latter effects have received more especially the name of detonators. Noble was the first to recognise the character of these when experimenting on nitroglycerin in 1864, and from thence he deduced the convenient method of exploding this substance effectually by means of a priming of mercury fulminate.

Gun-cotton does not present less variety. Abel has published, with reference to this matter, since the year 1868, some very curious experiments, which similarly tend to establish a great diversity between the conditions of deflagration in this substance according to the mode of detonating it.[1] Roux and Sarrau have generalised these phenomena by distinguishing what they have termed the explosions of the first and of the second order, a real distinction, yet one which appears insufficient, by reason of its too absolute character.

3. However strange this diversity may appear at first sight, the author holds nevertheless that thermo-dynamic theories are capable of accounting for it by a suitable analysis of the phenomena of shock.

In fact, the variety of explosive phenomena depends on the speed with which the reaction is propagated, and on the more or less intense pressures which result therefrom.

Take the simplest case, that of an explosion determined by the fall of a weight from a certain height. At first one would be inclined to attribute the effects observed to the heat disengaged by the compression due to the shock of the suddenly arrested weight. But calculation shows that the stoppage of a weight of several kgms. falling from a height of 0·25 metre or 0·50 metre cannot raise the temperature of the explosive mass more than a fraction of a degree, if the resultant heat be uniformly distributed throughout the entire mass. Such mass could therefore never reach to a high temperature, such as 190° and 200°, for instance, in the case of nitroglycerin, a temperature to which it would seem necessary to raise the entire mass suddenly in order to produce explosion.

It is by a different mechanism that the energy of the weight transformed into heat becomes the origin of the effects observed.

[1] "Comptes rendus des séances de l'Académie des Sciences," tom. lxix. pp. 105 à 121. 1869.

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It is sufficient to admit that pressures which result from the shock exercised on the surface of nitroglycerin are too sudden to distribute themselves uniformly throughout the whole mass, and that consequently the transformation of the energy into heat takes place more especially in the first layers reached by the shock. If this be sufficiently violent, these layers may thus be suddenly raised up to about 200°, and they will immediately decompose, producing a great quantity of gases. The production of gas is, in its turn, so sudden that the striking body has not time to displace itself, and the sudden expansion of the gases of the explosion produces a first shock, doubtless, more violent than the first on the layers situated below. The energy of this new shock changes itself into heat in the layers which it first reaches. It determines their explosion, and this alternation between a shock developing an energy which becomes changed into heat, and a production of heat which raises the temperature of the heated layers up to the degree of a new explosion capable of reproducing a shock, transmits the reaction from layer to layer throughout the entire mass. The propagation of the deflagration thus takes place by virtue of phenomena comparable to those which give rise to a sound wave; that is to say, by producing a true explosive wave which travels with a rapidity incomparably greater than that of a simple inflammation, induced by the contact of a body in ignition and effected in conditions under which the gases freely expand as they are produced. We shall define this explosive wave and study its characteristics in Chapter VII.

4. The reaction induced by a first shock in a given explosive substance propagates itself with a rapidity which depends on the intensity of the first shock, seeing that the energy of the latter transformed into heat determines the intensity of the first explosion, and consequently that of the entire series of consecutive effects. Now the intensity of the first shock may vary considerably according to the mode in which it is produced. The effect of the blow of a hammer may vary in its duration, for instance, from $\frac{1}{100}$ to $\frac{1}{10000}$ of a second, according to whether the blow be given with a hammer with a flexible handle, or with a block of steel, as shown by Marcel Deprez's experiments.

It follows, then, that the explosion of a solid or liquid mass may develop itself according to an infinite number of different laws, each of which is determined *cæteris paribus* by the original impulse. The more violent the initial shock, the more sudden will be the decomposition induced, and the more considerable will be the pressures exercised during the entire course of this decomposition. One single explosive substance may therefore give rise to the most diverse effects according to the process of ignition.

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5. Effects vary similarly according to whether the substance is pure or associated with foreign substances, and again according to the structure of the latter. This is shown by dynamite, a mixture of nitroglycerin with silica; which has lost a great part of its sensitiveness to ordinary shock, yet it remains explosive under the shock of a ball, and particularly under the shock of mercury fulminate.

6. Gun-gotton impregnated with water or paraffin becomes equally non-sensitive to a shock. In order to explode it a small supplementary cartridge of dry gun-cotton powder primed with fulminate must be employed.

If a small quantity of camphor be incorporated with nitrocellulose its susceptibility to explosion by shock is almost completely annihilated, at least at the ordinary temperature; to such an extent that this association constitutes a substance now employed for various purposes under the name of celluloid.

7. Blasting gelatin, which is made of nitroglycerin and nitrocotton, sometimes with the addition of camphor, constitutes an elastic mass very slightly sensitive to shock, and which in like manner requires an auxiliary cartridge of dry gun-cotton also primed with fulminate.

8. The change introduced by the camphor and resinous matters in the explosive properties of such substances, results from the modification supervening in the cohesion of the mass. The mass has acquired a certain elasticity and solidity of parts, by reason of which the initial shock of the detonator is at once propagated throughout a much larger mass (see p. 38). Besides, a portion of the effects of the shock is expended in the work of tearing up and separation, a small portion of it remains, which is susceptible of heating the parts directly struck, and this heating is, moreover, distributed throughout a large mass. Hence a sudden and local rise in temperature, capable of determining chemical and consecutive mechanical actions, becomes more difficult; it will require the employment of a detonator of much greater weight. This results from the preceding theory.

9. But camphor, on the other hand, should not, and does not, in fact, exercise, as experience proves, any specific action on a discontinuous powder, such as potassium chlorate powders. It is this which also explains the fact that blasting gelatin, when frozen, recovers a sensitiveness to shock which may be compared with that of nitroglycerin; the continuity of it has been destroyed by the crystallisation of this substance.

10. Hence we see the importance of primers, until recently regarded as simple agents intended to communicate flame to powder. In fact these primers, provided only their bulk be sufficient, regulate by their nature the character of the initial shock, and consequently the character of the entire explosion. In this case they take the name of detonators,

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properly so called. Pure mercury fulminate is especially employed in this respect; it is the most powerful of detonators, that is to say, its shock is more violent and more sudden than that of any other substance, which is explained by the suddenness of its decomposition, together with the extraordinary magnitude of the pressure which it would develop when detonating in its own volume (almost 26000 atm.). At page 52 a certain number of characteristic facts have been cited relative to this specific influence of primers. We shall return to this subject.

§ 7. Combustion and Detonation.

1. Progressive combustion has particularly preserved the name of *combustion;* the name *detonation* being reserved to almost instantaneous combustion with expansion of gas. From this, again, we get the distinction proposed by Sarrau between the explosions termed of the first order, such as those of black powder, which are really ordinary combustions, and the explosions termed of the second order, or detonations properly so called, such as that of nitroglycerin, produced by a strong priming of mercury fulminate.

Nevertheless, the facts known do not, in the author's opinion, compel us to admit a difference in the nature, and a line of absolute demarcation between the two orders of phenomena; they tend rather to place these latter under an aspect showing an indefinite variety comprised between two extreme limits:—

(*a*) The detonation of the explosive substance in its own volume reaching the maximum of temperature and pressure, and consequently the maximum of speed which chemical reaction realised under these conditions involves. This effect is produced when the substance retains the totality of its energy, that is to say, of the heat developed in the chemical transformation up to the moment when this latter propagates itself to the adjacent portions. Detonation is especially produced by a very sudden shock. Gases formed at the point where the shock is produced at first have not, so to speak, time to become displaced, and they immediately communicate their energy to the parts in contact; the action is thus propagated into the entire mass with a sort of regularity, producing in it a veritable explosive wave.

The velocities of propagation which have been measured with dynamite and compressed gun-cotton belong to this order of detonations, and they are very different from those of combustion of black powder. For instance, the Austrian artillerists have observed a velocity exceeding 6000 metres per second when detonating a dynamite cylinder 67 metres in length; Colonel Sébert has observed velocities of 5000 to 7000 metres (a mean velocity of 6138 metres) in pulverulent gun-cotton compressed

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into long leaden tubes. Further on it will be seen that the author, together with M. Vieille, has measured velocities of several thousands of metres per second in explosive gaseous compounds.

(*b*) Progressive combustion transmitting itself, step by step, under the conditions in which the cooling due to conductivity by contact with inert substances, etc., lowers the temperature to the lowest degree compatible with the continuation of the reaction; all heat is thus dissipated with the exception of a very small fraction necessary to propagate the reaction in the adjacent parts. The velocity of combustion in explosive gases measured by Bunsen (p. 49) is attributable to this mode of inflammation.

In the case of solid or liquid explosives the propagation of simple inflammation is rendered more difficult by the movement of the gases, which distribute themselves throughout a large space around the point inflamed, instead of acting in a volume equal to, or slightly different from that of the original bodies; they thus share their temperature with a large mass of the substance up to such a point that the latter cannot be raised to the desired degree for it to commence decomposition. Thus we often see the substance dispersed by the gases without experiencing total combustion, and even without undergoing any change. This happens particularly with explosive substances not confined within an envelope which concentrates the action of the gases and gives to it a common resultant (p. 40).

This is the case with nitroglycerin, which is found unaltered in the vicinity of progressive deflagrations, and it also occurs with dynamite placed on the ground in a thin layer. Damp gun-cotton, which is not inflammable, has also furnished numerous instances of this dispersion resulting from the use of an insufficient detonator. It is by reason of this special action of gases that a simple inflammation of a dynamite cartridge, owing to the use of a badly placed fuse or of fulminate not in sufficiently close contact, should be avoided, inflammation thus preceding the direct action, which ought to be produced in immediate contact with the fulminate.

2. Between these two limits an entire series of intermediate states are observed, and they are unlimited in number as the various modes of inflaming dynamite demonstrate. This is proved by the influence of a sufficiently strong tamping (p. 40), which transforms an inflammation into a true detonation.

Finally, we might here cite the inequality of the effects produced by successive explosions of charges of the same agent detonating by influence at limiting distances beyond which the explosion would no longer propagate itself (see further on).

This variety in the phenomena is due to two orders of causes,

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the one being mechanical and the other more particularly chemical.

3. From a mechanical point of view it is conceivable that between the two limits of progressive combustion and detonation the intermediate modes of propagation and reaction may, according to circumstances, be produced (p. 53), combustion tending to transform itself more or less quickly into detonation. But only the two limits should be regarded as constituting regular standards. This will be more fully defined in the chapter relating to the explosive wave.

4. Chemical phenomena themselves may vary, at any rate under certain conditions. In fact, the mode of decomposition is not unique, unless the explosive substance contains sufficient oxygen to cause a total combustion, as happens in the case of nitroglycerin and nitromannite. It is further essential that this total combustion should have really taken place; which does not necessarily occur, especially in slow inflammations, effected at as low a temperature as possible and in which incomplete reactions may at first become developed.

5. But it often happens that oxygen is deficient, or that the first reaction gives rise to a bad distribution of this oxygen, as in the case where nitroglycerin burns slowly, producing a nitrous vapour, and fixed or gaseous matters, incompletely burned. Under these circumstances the possible decompositions are manifold; their number depends on the temperature, on the pressure, and on the quickness of the heating. We have already pointed out this case for ammonium nitrate (p. 6); it is generally observed in organic substances decomposable by heating.[1] Mixtures such as black powder are equally susceptible of it.

6. Among the numerous decompositions of the same substance, those which develop the greatest heat are those which also generate the most violent explosive effects, all things else being equal. This is evident, since the volume of gases (reduced to 0° and 760 mm.) reaches its maximum value at the same time. But it takes place in other cases, the decomposition being always followed by a diminution of pressure, as has been elsewhere shown (p. 8).

On the other hand, these are not generally the reactions which manifest themselves at the lowest temperature possible. If, therefore, the explosive body receive in a given time a quantity of heat which is insufficient to carry its temperature up to a degree which corresponds to the most violent reactions, it will experience a decomposition capable of disengaging less heat, or even of absorbing it; and it will by this decomposition become completely destroyed without developing its most energetic effects.

[1] "Essai de Mécanique Chimique," tom. ii. p. 45.

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The contrary will happen if the body be rapidly heated up to the temperature corresponding to the most energetic reaction.

7. In fine, the multiplicity of possible reactions involves a complete series of intermediate phenomena, especially as, according to the mode of heating, it may happen that several decompositions will succeed one another progressively. This succession of decompositions gives place to effects even more complicated, as Jungfleisch has pointed out, when the first decomposition, instead of producing a total elimination of the decomposed part (changed into gaseous or volatile substances), results in a division of the primitive substance into two parts; the one gaseous, which becomes eliminated, and the other solid or liquid, which remains exposed to the consecutive action of heating. The composition of this residue being no longer the same—which happens, for instance, with nitroglycerin which has at first disengaged a portion of its oxygen in the form of nitrous vapours—the effects of its consecutive destruction may be completely changed.

8. Such are the causes, some chemical, some mechanical, owing to which nitroglycerin and compressed gun-cotton each produce such different effects, according as they are inflamed by the aid of a body feebly ignited by a flame, by an ordinary fuse, or again by the aid of a cap charged with mercury fulminate.

For example, Roux and Sarrau have found that the necessary charges for breaking a bomb shell, vary *cæteris paribus*, in an inverse ratio to the following numbers, the value of which is calculated by taking gunpowder as unit.

	Detonation.	Inflammation.
Nitroglycerin	10·0 ...	... 4·8
Compressed gun-cotton	6·5 ...	... 3·0
Picric acid	5·5 ...	... 2·0
Potassium picrate	5·3 ...	... 1·8

The weight of the bursting charge with black powder, itself under the influence of nitroglycerin primed with fulminate, has been reduced in the proportion of 4·34 to 1.

This inequality in the force of the same powder according to the method of ignition, is also partially attributable to the cooling produced by the walls in a slower reaction; but generally it results from a change occurring in the chemical reaction.

9. The diversity of the effects is less marked with non-compressed gun-cotton, because the influence of the initial shock is exercised on a smaller quantity of matter, and particularly because the propagation of the successive reactions in the mass develops therein weaker initial pressures and a less direct transformation of energy into heat transmitted to the explosive body. The cause of this is the interposed air. Consequently

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the explosive wave can only be produced with difficulty in such a substance.

Compressed gun-cotton itself is less compact than nitroglycerin owing to its structure. This is the reason why pressures which are due to shocks should become sensibly attenuated by the existence of interstices. Gun-cotton is therefore more difficult to explode than nitroglycerin. Nitroglycerin explodes by the fall of a weight from a lesser height, by the use of a priming charged with gun-cotton, or a mixture of fulminate and potassium chlorate, etc.; whereas gun-cotton does not explode under the influence of nitroglycerin, nor under the influence of a mixture of fulminate and chlorate, it requires the more sudden shock of pure mercury fulminate.

This latter agent is also less efficacious if it be employed exposed than if it be placed in a thick copper or tin covering; it is less efficacious in an envelope made of paper or tinfoil, than in a copper envelope; it is still less efficacious if the priming be not in contact with the gun-cotton. Finally, if it be placed in a leaden tube, an elastic substance which at once yields to pressure, its effect becomes nullified.

Nitroglycerin is less explosive under the influence of a priming of fulminate if it be inflamed before the explosion of the fulminate, the previous inflammation producing a certain void between the two (p. 56). The absence of immediate contact between the dynamite contained in the cartridges and the priming of fulminate is prejudicial for the same reason, the shock being partially deadened by the interposed air. The sensitiveness to the action of the fulminate is greater in dynamite, containing liquid nitroglycerin, than in that containing frozen nitroglycerin, which is similarly explained by the absence of homogeneity in congealed dynamite, in which nitroglycerin is partially separated from the porous silica owing to its solidification.

10. All these phenomena are explained by the more or less considerable value of initial pressures, by their more or less sudden development, and by their more or less easy communication to the rest of the mass; that is to say, by the conditions which regulate the energy transformed into heat in a given time in the interior of the first layers of the explosive substance which are reached by the shock (see pp. 52, 53).

The quantity of energy thus transformed depends therefore both on the suddenness of the shock, and on the greatness of the work which it is capable of developing. Now here we have two data, which vary with each explosive substance. For instance, the most suitable primings are not always those in which the explosion is the most instantaneous. Abel has recognised that nitrogen chloride is not very efficacious in inflaming gun-cotton; nitrogen iodide, so sensitive to the least

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friction, remains absolutely powerless with gun-cotton. Now nitrogen chloride is precisely one of the explosive bodies of which we are treating here, which develop the least heat consequently the least work, for a given weight, owing to the high figure of the equivalent of chlorine. We therefore see that it is necessary to use more of it by way of priming. As to nitrogen iodide, according to the analogies taken from iodo-substitution compounds,[1] and from the great weight of the equivalent of iodine, its explosion should develop much less heat and much less work for the same weight than even nitrogen chloride; its impotence is therefore easily understood.

§ 8. Combustion effected by Nitric Oxide.

It is advisable to consider here the conditions which determine the commencement of reactions, conditions which are of fundamental importance in the study of explosive substances and on the knowledge of which the study of the combustion effected by nitric oxide throws a very special light.

1. Nitric oxide contains more than half its weight of oxygen, and this oxygen, in connection with a combustible body, disengages 21,600 cal. more than free oxygen (O = 16 grm.). It therefore seems that nitric oxide should be a more active burning agent than free oxygen. Nevertheless, this only happens under peculiar circumstances, noticed by chemists from the commencement of the nineteenth century, which have given rise to experiments, which are produced in every course of lectures, but have not as yet been properly explained. The author has resumed this study, which appears to throw a good deal of light on the work which precedes reactions, and on the manifold equilibriums of which one and the same system is susceptible.

2. Let us place in the presence of free oxygen two gases susceptible of combination with it, in the same proportions of volume, such as nitric oxide and hydrogen previously mixed in equal volumes, $NO_2 + H_2 + O_2$, nitric peroxide is immediately formed, hydrogen being unaffected (*respecté*). This preference is manifested, evidently, owing to the inequality of the initial temperature of the two reactions, nitric peroxide being formed in the cold; whereas water is produced only at about 500° to 600°.

3. Nevertheless, this explanation is less decisive than it appears to be, since the combination of nitric oxide and hydrogen liberates a great quantity of heat (1900 cal.), say two-thirds of the heat of formation of gaseous water (29,500 cal.). Now this heat should raise the temperature of the system to the degree at which oxygen and hydrogen combine.

In order fully to demonstrate the phenomenon, the experi-

[1] "Annales de Chimie et de Physique," 4e série, tom. xx. p. 449.

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ment was repeated, doubling the quantity of oxygen, so that the proportion of this element sufficed for the combustion of the hydrogen and also nitric oxide.

The reaction produced under these conditions does not give rise to the combustion of hydrogen, the nitric peroxide being formed alone, whether the nitric oxide be introduced into the mixture made beforehand of oxygen and hydrogen, or the oxygen be introduced into a mixture previously formed of hydrogen and nitric oxide.

Now the temperature developed by this formation would be 927°, according to the calculation based on the known specific heats of the elements, and supposing that of the nitric peroxide to be equal to the sum of its components. It seems difficult to explain these facts, except by supposing the real temperature to be much lower; that is, by attributing to the nitric peroxide a specific heat greater than that of the elements, as is the case with the chlorides of phosphorus, arsenic, silicon, tin, titanium, etc., in the gaseous state,[1] and probably increasing with the temperature, as in the case of carbonic acid.

This has, in fact, been verified experimentally by the author and M. Ogier.[2] The temperature, calculated according to these new data, falls to 700°, and even lower.

There is, moreover, no exceptional property of the nitric oxide to prevent combustion. In fact, if the inflammable temperature of a mixture of oxygen and combustible gas, such as oxygen and phosphoretted hydrogen, be notably lower, it will suffice to introduce a few bubbles of nitric oxide, in order to ignite it at once.

4. When these experiments, with a mixture of hydrogen and nitric oxide, are carried out over mercury, a complication takes place which corresponds to a new distribution of the oxygen, the mercury intervening as a third combustible body, forming basic nitrates and nitrites.

The quantity of oxygen absorbed is almost double, but the hydrogen remains unconsumed.

5. These facts being admitted, let us see what happens when we try to ignite a mixture of hydrogen and nitric oxide. Berthollet and H. Davy found that ignition does not take place, either under the influence of the electric spark, or the influence of a body in a state of combustion. Further, a lighted match is extinguished in a similar gaseous mixture. If sometimes the hydrogen of this mixture becomes ignited, it is outside the test tube and at the expense of the oxygen in the atmosphere.

Nevertheless, the flame of the match, or the electric spark, brings about, at the point heated, decomposition of nitric oxide

[1] "Essai de Mécanique Chimique," tom. I. pp. 336 and 400.

[2] "Bulletin de la Société Chimique," 2e série, tom. xxxvii. p. 335.

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into its elements; for this decomposition takes place at from 500° to 550°, according to the author's experiments.[1] But the oxygen is gradually taken up by the surplus of oxide, without uniting in any notable proportion with the hydrogen, as has been shown.

6. The reaction between hydrogen and nitric oxide takes place, however, when it is excited by a series of sparks, but gradually and locally. In fact, at the end of ten minutes the mixture of nitric oxide and hydrogen in equal volumes, NO + H_2, was reduced to one half in these conditions. After some hours the nitric oxide had disappeared, but there remained several hundredth parts of free hydrogen, and a basic salt had been formed at the expense of the mercury. This latter formation proves that the oxygen set free by the sparks was seized, to a fractional extent, by the nitric oxide to produce nitric peroxide, a gas, the presence of which was quite manifest. This nitric peroxide gas, in its turn, is partially destroyed by the hydrogen under the influence of the spark, whilst another portion oxidises the mercury, and thus a portion of the oxygen is withdrawn from the ulterior reaction of the hydrogen.

In a word, the formation of nitric peroxide is intermediate between the decomposition of the nitric oxide and the oxidation of at least a portion of the hydrogen. We have then,—

(1) $NO = N + O$.
(2) $NO + O = NO_2$.
(3) $NO_2 + 2H_2 = 2H_2O + N$.

Therefore, in order that the hydrogen may be regularly oxidised, it is not the nitric oxide which it is necessary to decompose, but the nitric peroxide, a very stable compound, the destruction of which requires an extremely high temperature. This accounts for the fact that the combustion induced by flame or electric sparks is not propagated.

7. The same experiments were repeated with a mixture of nitric oxide and carbonic oxide:

$$NO + CO.$$

According to W. Henry, this mixture is also not ignited by a lighted match, which is extinguished in it, nor by electric sparks.

Nevertheless, it was observed that a series of sparks continued during some hours decomposed it completely. Only half of the carbonic oxide is thus converted into carbonic acid, and the combustion is so imperfect that a little carbon is precipitated on the platinum wires, as if pure carbonic oxide had been employed. The surplus oxygen of the oxide forms first of all nitric peroxide, and then basic salts of mercury.

Here again, the temperature produced by the spark was

[1] "Annales de Chimie et de Physique," 5e série, tom. vii. p. 197.

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sufficient to burn the carbonic oxide, but all round the path of the spark the temperature fell rapidly to a point at which it could still decompose the nitric oxide, without igniting the carbonic oxide.

The oxygen formed at the expense of the former compound thus produced nitric peroxide gas with the surplus.

8. The contrast will be remarked between this experiment and the sudden combustion of carbonic oxide produced by mercury fulminate detonating in nitric oxide (see further on). The fact is that the latter agent sets free at once all the oxygen of the oxide without passing through the state of nitric peroxide.

9. Let us examine more closely the list of gases and other bodies capable of burning direct at the expense of the nitric oxide by simple inflammation, or electric sparks, and seek the causes of the difference which exists between the reaction of these bodies and of those which do not burn immediately.

The following do not ignite :—

Nitric oxide and hydrogen in equal volumes,

$$NO + H_2.$$

Nitric oxide mixed in the same way with carbonic oxide,

$$NO + CO.$$

Nitric oxide mixed with marsh gas,

$$4NO + CH_4.$$

Nitric oxide mixed with methyl chloride,

$$3NO + (CH_3Cl).$$

And even nitric oxide mixed with methylic ether,

$$6NO + (CH_3)_2O.$$

The combination of these mixtures does not take place by contact with a small flame, nor under the influence of electric sparks.

Sulphur also, when simply ignited, is extinguished in nitric oxide.

This absence of combustion is especially remarkable with methylic ether, which takes the same quantity of oxygen and disengages nearly the same quantity of heat as ethylene, a gas which burns, on the contrary, at the expense of the nitric oxide. The two mixtures occupy, moreover, the same volume.

10. On the other hand, the contact of a lighted match ignites the following mixtures when formed according to equivalent ratios of volume:—

Nitric oxide mixed with cyanogen,

$$2NO + CN.$$

Nitric oxide mixed with acetylene,

$$5NO + C_2H_2.$$

Nitric oxide mixed with ethylene,

$$6NO + C_2H_4.$$

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These combustions, started by a small flame in a test tube, are gradual and progressive, and only produce very feeble explosions like that of carbonic oxide and oxygen.

By means of a powerful electric spark combustion also takes place, and with singular violence, which shows the difference in the mode of propagation of the chemical action.

Here it may be mentioned that phosphorus burns briskly in nitric oxide, that the same takes place with boiling sulphur, with carbon previously made incandescent, and that carbon bisulphide also burns briskly in this gas; these are well-known experiments.

11. The principal cause of these diversities is the difference in the temperatures developed by the combustible bodies burning at the expense of the nitric oxide.

The theoretical calculation of these temperatures may be made by admitting, in the ordinary way, that the specific heat of a compound gas is equal to the sum of its elements, and that each of the latter taken at its molecular weight possesses the same specific heat as hydrogen, that is, 6·8 for H_2 = 2 grms. at constant pressure. Temperatures thus calculated are certainly not the real temperatures, yet it may be admitted that the order of relative amounts is the same, and that is sufficient for our comparisons.

Mixtures which do not ignite.

	Theoretical temperature of combustion.
$NO + H_2$ (water, gaseous)	5900°
$NO + CO$	6600°
$3NO + CH_3Cl$ (water, gaseous)	5700°
$4NO + CH_4$ (water, gaseous)	6300°
$6NO + (CH_3)_2O$ (water, gaseous)	6000°
$2NO + S$ taken at 15°	6600°

Mixtures which do ignite.

	Theoretical temperature of combustion.
$2NO + CN$	8500°
$5NO + C_2H_2$ (water, gaseous)	8700°
$6NO + C_2H_4$ (water, gaseous)	7400°
$6NO + CS_2$	7500°
$2NO + C$	8200°
$5NO + P_2$	10200°
$4NO + PH_3$	8400°
$2NO + S$ previously heated to 450° ...	7050°

It will be observed that the theoretical temperature of combustion of sulphur, taken at about 15° by nitric oxide, is very near the limit; it therefore does not burn. On the contrary, if the sulphur be contained in a heated receptacle and kept at a temperature of about 450° by boiling, the nitric oxide being rapidly raised by contact with the vessel to about the same temperature, and thus the temperature of combustion of the

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mixture be raised, then the sulphur should burn in nitric oxide.[1]

This is what is noticed, as we know, in operating with sulphur placed in a small crucible previously brought to a red heat.

The temperatures of combustion estimated in this way are generally very near those estimated by the employment of free oxygen, the excess of heat produced by the decomposition of nitric oxide being compensated by the necessity of heating the nitrogen. All these figures, however, do not express absolute values, yet they may be regarded as marking the relative order of temperatures of combustion.

12. This table, understood in this manner, shows that the property of burning at the expense of nitric oxide under the influence of a flame or electric spark, depends more especially on the temperatures developed. The comparison of ethylene with methylic ether is particularly decisive in this respect, since the relations of volume between the combustible and the combustive gas are exactly the same, and the heats disengaged (451,100 cal. and 443,800 cal.) do not sensibly differ, but methylic ether also contains the elements of water, which lowers the temperature of combustion.

In short, among the bodies comprised in the table, none of those which develop a theoretical temperature below 7000° will ignite, whereas all the bodies which develop a higher temperature either burn or detonate. It is possible that this circumstance is connected with the previous formation of nitric peroxide at the expense of nitric oxide (see p. 62), and consequently with the necessity for a very high temperature in order to regenerate, at the expense of the nitric oxide, the oxygen which is indispensable to combustion.

13. Instead of destroying nitric peroxide by heating it to an excessively high temperature, it can be decomposed by a chemical reaction at a lower temperature, which lowers the theoretical limit of the temperature of combustion.

This is precisely what happens in the case of ammonia gas. This gas, in fact, mixed with nitric oxide,

$$3NO + 2NH_3,$$

ignites with a match, and, according to W. Henry, detonates under the influence of the electric spark. The theoretical temperature of combustion of the mixture (5200°) is, however, less than all the foregoing temperatures. But, on the other hand, nitric peroxide reacts even when cold on ammonia gas, and the reaction develops itself still more simply by the introduction of oxygen into a mixture of nitric oxide and of ammonia gas. When cold it will produce both nitrogen and ammonium

[1] "Essai de Mécanique Chimique," tom. i. p. 331.

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nitrate,[1] which at a high temperature resolves itself into nitrogen and water. Therefore we definitely obtain

$$2NO + O + 2H_3N = 4N + 3H_2O \text{ disengages (water, gaseous)} + 98{,}000 \text{ cal.}$$

Every portion of nitric oxide destroyed by the spark with the formation of free oxygen, determines, therefore, a new reaction which disengages heat, and easily propagates the combustion of the system, which does not take place in gases which do not exercise a special reaction on nitric peroxide.

§ 9. Decomposition of Endothermal Combinations, Acetylene, Cyanogen, etc.

1. So far, we have treated more especially of the combustion and detonation of mixtures and combinations containing such combustible elements as carbon, hydrogen, sulphur, and the combustive elements such as oxygen. But as the theories which we are considering are based essentially on the disengagement of heat and the development of the gases produced by transformation, they lead to consequences of a very special character, which are very interesting as regards the decomposition of endothermal combinations such as acetylene, cyanogen, and nitric oxide.

Acetylene, cyanogen, and nitric oxide are, in fact, formed from their elements with the absorption of heat. This absorption amounts to

$A - 61{,}100$ cal.[2] for acetylene ($C_2H_2 = 26$ grms.)
$A - 74{,}500$ cal. for cyanogen ($2CN = 52$ grms.)
$A - 31{,}600$ cal. for nitric oxide ($NO = 30$ grms.)

If we succeed in rapidly decomposing these gases into their elements, such a quantity of heat reproduced inversely will raise the temperature up to 3000° in acetylene and nitric oxide, up to 4000° in cyanogen, according to a calculation founded on known specific heats of the elements.

The proper figures for this calculation are as follows. We will admit for the mean specific heat of carbon $C_2 = 24$ grms., the value 12; for that of hydrogen $H_2 = 2$ grms., 6·8 at constant pressure, and 4·8 at constant volume, these latter values being equally applicable to nitrogen $N_2 = 28$ grms., and to oxygen $O_2 = 32$ grms. at the same volume. We thus find,

For acetylene decomposed under constant pressure 3300°, under constant volume 3640°.

For cyanogen decomposed under constant pressure 3960°, under constant volume 4375°.

[1] See author's remarks, "Annales de Chimie et de Physique," 5e série, tom. vi. p. 208.

[2] This figure refers to carbon as diamond; in amorphous carbon such as is precipitated at the time of decomposition we should obtain 6000 cal. less. The same remark applies to cyanogen as the mean specific heat of carbon.

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For nitric oxide decomposed under constant pressure 3200°, under constant volume 4500°.

It is understood that the calculation of these temperatures is subordinate to the presumed constancy of the specific heats. Whatever opinion is held in this respect it is certain that it gives an idea on temperature more probable in the present case, where it is a question of an elementary decomposition, than in reactions in which compound bodies are formed, such as in the combustions of hydrogen or carbonic oxide, combustions which are limited in their progress by the dissociation of compound bodies.

2. However, it has not been possible up to the present to effect the explosion of acetylene, or cyanogen, or of nitric oxide.

Whereas hypochlorous gas detonates under the influence of slight heat, when in contact with a flame, or a spark, in spite of the smaller amount of heat liberated, + 15,200 cal. (for Cl_2O = 87 grms.), which can only raise the elements of this gas to 1250°, on the other hand, acetylene, cyanogen, and nitric oxide do not detonate either by simple heating or by contact with flame, nor even under the influence of the spark or even the electric arc.

These differences are important. The diversity which exists between the mode of destruction of endothermal combinations is due in each given reaction to the necessity of a kind of preparation, and a certain amount of preliminary work. The author has, besides, examined [1] the characters and the generality of this preliminary work in the production of chemical reactions. Now the work necessary for resolving the compounds named into the elements does not appear to consist in a simple heating, slow and progressive in its nature, at least within the limits of the temperature above pointed out. In fact, acetylene, cyanogen, and nitric oxide never explode, as far as the author's experience goes, no matter to what temperature they are raised.

It is not that these compound gases are absolutely very stable—they in fact decompose frequently, and even according to experience at a dull red heat, either with the formation of polymers (benzene by acetylene), or with a fresh distribution of their elements (nitrogen, monoxide, and nitric peroxide, by nitric oxide) [2]—but they do not explode in spite of the very great liberation of heat accompanying these changes, probably by reason of the slowness of their action, nor do they explode, which is stranger still, under the influence of electric sparks, in spite of the excessive and sudden heat which these latter develop. Carbon, however, on the passage of the sparks, is precipitated at once from acetylene or cyanogen, while hydrogen and nitrogen

[1] "Essai sur la Mécanique Chimique," tom. ii. p. 6.

[2] "Annales de Chimie et de Physique," 5e série, tom. vi. p. 198.

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are liberated. The electric arc accelerates in a peculiar degree the decomposition of the cyanogen in which it is produced, yet without rendering it explosive.[1] Nitrogen and the oxygen of the nitric oxide also separate on the passage of the electric spark. As a matter of fact the oxygen of this latter gas becomes united with the excess of the surrounding oxide and generates nitric peroxide. A portion of the hydrogen and of the carbon liberated at the expense of the acetylene also reunites under the influence of the electricity so as to reconstitute this hydrocarbon, the whole forming a system in equilibrium.[2] To these circumstances might be attributed the absence of the propagation of the decomposition, but this explanation is not sufficient for the cyanogen, which becomes entirely decomposed,[3] without possibility of reconversion.

Nor does this suffice for arseniuretted hydrogen, a gas decomposable, according to Ogier, with liberation of 36,700 cal. (AsH_3 = 78 grms.).

This latter gas is so very unstable that it is continually decomposing at normal temperature, if kept in sealed glass tubes. It is well known with what facility even the last trace is decomposed by heat in Marsh's apparatus. A series of electric sparks will also completely destroy it. Nevertheless, arseniuretted hydrogen does not explode, as the author has shown, either under the influence of progressive heat or under that of the electric sparks.

3. Thus, in the endothermal combinations already enumerated, there exists a condition, associated with their molecular constitution, which prevents the propagation of the chemical action under the influence of mere progressive heating or of the electric spark, at least so long as the temperature remains below certain limits.

We are aware that the study of explosive substances presents circumstances which are analogous. The simple ignition of dynamite, for instance, would not suffice to cause its explosion; on the contrary, Nobel has shown that explosion is produced by the influence of special detonators, such as mercury fulminate, and which are susceptible of developing a very violent shock. The thermodynamic theory has already been given (p. 53) of these effects, which appear to be due to the formation of a veritable explosive wave, which wave is totally distinct from the sonorous waves, properly so called, since it results from a certain cycle of mechanical, calorific, and chemical actions, which reproduce themselves step by step, transforming themselves one into the other; this is shown in the experiments which the

[1] "Comptes rendus des séances de l'Académie des Sciences," xcv. p. 955.

[2] "Annales de Chimie et de Physique," 4e série, tom. xviii. pp. 160, 199.

[3] That is, it does not contain any trace of a hydrogenated body susceptible of forming hydrocyanic acid, which, on the contrary, gives rise to equilibrium.

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author made, together with Vieille, on mixtures of hydrogen and other combustible gases with oxygen. It has in like manner been shown that the great effectiveness of mercury fulminate as a detonator is explained, not only by the rapidity of decomposition in this body, but more particularly by the enormous pressure which it develops when exploding in its own volume, pressures far above those of all known bodies, and which may, according to our tests, be estimated at over 27,000 kgms. per sq. cm.

This led to the detonation being attempted of acetylene, cyanogen, and arseniuretted hydrogen under the influence of mercury fulminate, and the trials were completely successful. The following are the details.

4. *Acetylene.*—Introduce a certain volume of acetylene, from 20 c.c. to 25 c.c., for instance, into a small test tube, E, the walls of which should be very thick. In the centre of the gaseous mass place a small cartridge, K, containing a small quantity of fulminate (about 0·1 grm.), and traversed by a very thin metallic wire in contact at the other end with the iron fitting of the test glass, an electric current will bring this wire to a red heat. All this is supported by a tube containing a second wire fused into the tube, and extending outwards as far as F. The capillary glass tube CC, in the form of an inverted syphon, is fixed into a plug D, which closes the test tube.

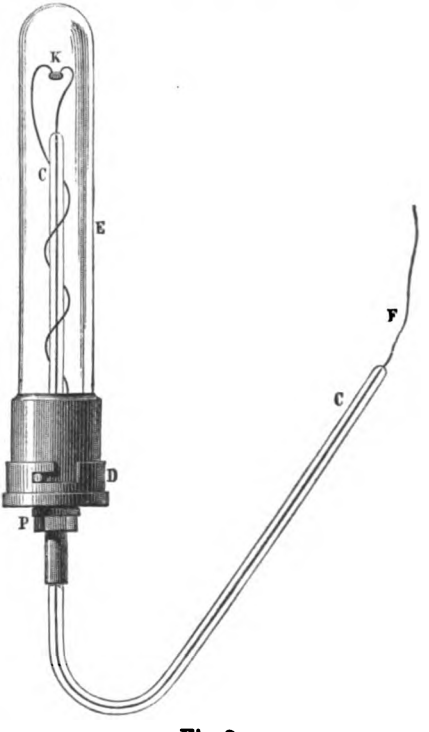

Fig. 3.

Fig. 3 shows the system in readiness; Fig. 4 shows the glass tube provided with its inner wire.

Fig. 5 shows the steel plug in its natural size, with the hole T, into which the above-named cap is screwed.

Fig. 6 gives in its natural size the steel cap P, through which there is a passage for the tube, which is cemented into this cap along with the second wire.

This arrangement will permit of the test tube being filled

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with gas over mercury, and of there introducing the wires fitted with their fuses and adjusted to the plug. This is then closed by a bayonet fastening, and the detonation is effected under a constant volume.

For this purpose, the current is passed; the fulminate goes off, a violent explosion is caused, and a large flame appears in the test tube. After cooling, the glass will be found filled with black finely divided carbon, the acetylene has disappeared, and free hydrogen remains.[1] Unscrew the cap P under the mercury, remove it with the capillary tube, and then collect and examine the gases contained in the test tube.

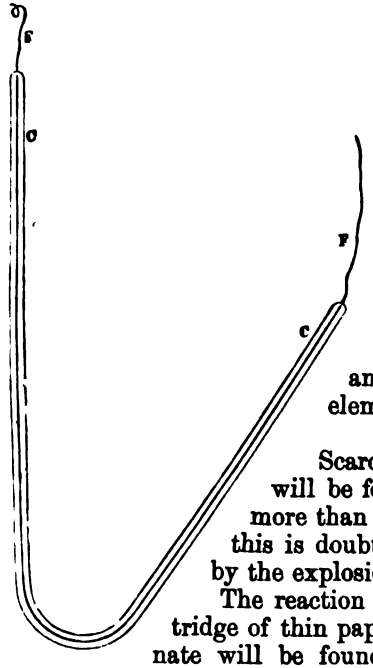

Fig. 4.

The acetylene is thus purely and simply decomposed into its elements—

$$C_2H_2 = C_2 + H_2.$$

Scarcely a trace of the original gas will be found, and, if any, it will not be more than a hundredth of a cub. cm., and this is doubtless some portion not reached by the explosion.

The reaction is so rapid that the small cartridge of thin paper which enveloped the fulminate will be found torn, but not burned, even in its thinnest fibres; and this is explained, if we note that the time during which the paper remained in the explosion centre was about $\frac{1}{30,000,000}$ of a second, according to the thickness of the paper and the known data relative to the rapidity of this order of decomposition.

The carbon set free exhibits the same general conditions as that obtained in a tube at a red heat; it is mainly amorphous carbon, and not graphite; it dissolves almost totally when treated several times with a mixture of fuming nitric acid and potassium chlorate. Nevertheless, in this way, it gives a trace of graphite oxide, which proves that it contains a trace of graphite, produced doubtless by the transformation of the amorphous carbon under the influence of the excessive temperature to which it has been subjected.

The author has, in fact, shown that amorphous carbon heated up to about 2500° by electrolytic gas commences to change into

[1] Mixed with nitrogen and carbonic oxide proceeding from the fulminate, and which have been formed independently.

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graphite, and that the lamp-black precipitated by the incomplete combustion of the hydrocarbon also contains a trace of it.[1]

5. *Cyanogen.*—The same test carried out with cyanogen is

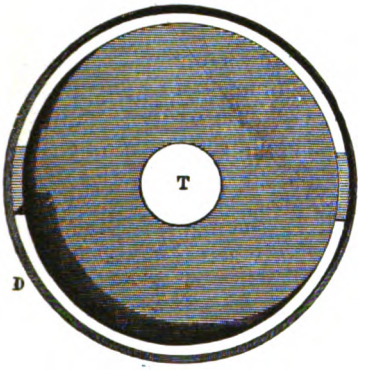

Fig. 5.

Fig. 6.

equally successful; the cyanogen detonates under the influence of the fulminate, and resolves itself into its elements.

$$2CN = C_2 + N_2.$$

Thus we can produce free nitrogen, and amorphous carbon in a highly divided state similar to what is obtained by the electric spark. This carbon marks paper as plumbago will do. Yet it is by no means real graphite, because it will almost totally dissolve, if repeatedly treated with a mixture of fuming nitric acid and potassium chlorate. Still one trace of graphitic oxide, left as a residue, bears witness to the existence of a trace of graphite, as in the case of acetylene.

This test is not always successful. Sometimes the explosion of the fulminate takes place without precipitating the carbon of the cyanogen.

Nitro-diazobenzene, which was also tested by using it as a detonator instead of fulminate, decomposed without causing the cyanogen to explode. Even the mode of decomposition of

[1] "Annales de Chimie et de Physique," 5e série, tom. xix. p. 418. The voltaic arc produces a more complete transformation; but then the effects of the heat become complicated by those of electricity (p. 419).

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nitro-diazobenzene was different under circumstances in which the detonator is destroyed at a slight pressure, from its decomposition in the calorimetric bomb under a high pressure, as observed by Vieille and the author. Instead of obtaining all the oxygen from the compound in the state of carbonic oxide at the same time as free nitrogen and a nitrogenous carbon of a very porous and dense nature, on this occasion, along with the nitrogen, only one-fourth of the volume of the theoretical carbonic oxide was observed, along with some phenol and a tarry substance.

6. *Nitric oxide.*—This body explodes under the influence of mercury fulminate, but the phenomenon is more complicated than with the former gases, the carbonic oxide produced by the fulminate burning, at the expense of the oxygen of the nitric oxide, to form carbonic acid. This combustion appears to have taken place at the expense of free oxygen, and not of nitric peroxide formed transitorily. In fact, the mercury is not attacked, contrarily to what always happens when this gas appears for a moment.

We therefore have,

$$NO = N + O$$
$$CO + O = CO_2.$$

The combustion even of carbonic oxide is characteristic, for nitric oxide, mixed with carbonic oxide, does not explode either by simple inflammation, or by the electric spark.

7. *Arseniuretted hydrogen.*—Arseniuretted hydrogen has exploded under the influence of the fulminate, and has become absolutely resolved into its elements, arsenic and hydrogen.

$$AsH_3 = As + H_3.$$

8. Here will be given experiments on the sudden decomposition of nitrogen monoxide into nitrogen and oxygen. This decomposition, which liberates + 20,600 cal. (N_2O = 44 grms.), may be caused by the sudden compression of 30 c.c. of this gas reduced to $\frac{1}{500}$ of their volume by the sudden fall of a ram weighing 500 kgms.[1]

On the other hand, nitrogen monoxide only decomposes gradually under the influence of progressive heat or of electric sparks.

9. All these tests are in reference to gases. But solid or liquid endothermal combinations offer the same variety. While nitrogen chloride and iodide explode under the influence of a slight heat, or of slight friction, nitrogen sulphide requires to be heated up to 207°, or requires violent concussion, in order to explode and to become resolved into its elements. It then liberates + 32,300 cal. (NS_2 = 46 grms.), according to tests which the author has made along with Vieille.

[1] "Annals de Chimie et de Physique," 5e série, tom. iv. p. 145.

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10. Potassium chlorate, itself a body which liberates + 11,000 cal. ($KClO_3$ = 122·6 grms.) when decomposing into oxygen and potassium chloride, may undergo this decomposition at an ordinary temperature, if struck violently with a hammer on an anvil, after being enveloped in a thin sheet of platinum. It has been found, in fact, that in this way an appreciable quantity of chloride is found. Pure chlorate, in a state of fusion, explodes much more easily, and sometimes of itself, if the heating be too sudden. This detonation has been the cause of more than one accident in laboratories.

11. As a further instance may be mentioned celluloid (a variety of nitro-cotton, mixed with various substances). At ordinary temperatures it is a very stable substance. The author, however, observed that this body explodes when brought up to the temperature at which it softens, and in this state struck with a hammer on an anvil.

Generally speaking, compounds and explosive mixtures become more and more sensitive to shocks in proportion as they approach the temperature of their initial decomposition (see p. 37).

12. Two other experiments were made, which it may be useful to point out, in spite of their negative character. One of them consisted in exploding the fulminate in an atmosphere of gaseous chlorine. Assuming the compound nature of chlorine regarded as an endothermal radical containing oxygen, one would have been able to observe the products of the decomposition caused by the explosion of the fulminate, yet the results were negative, as, of course, was to be expected, in accordance with received ideas. The chlorine had scarcely been introduced into the atmosphere when the fulminate exploded of itself, yet the chlorine was not destroyed.

This gas having been subsequently absorbed by agitating it with mercury, carbonic oxide and nitrogen remained in the proportion of gaseous volumes answering to the fulminate; that is to say, without any excess of carbonic acid, or of any other product formed at the expense of the chlorine.

13. An attempt was also made to destroy glucose, on the assumption that fermentations are exothermal operations.[1] A strong capsule of fulminate, containing 1·5 grms. of this body, was exploded in a metallic cartridge completely filled with an aqueous 20% solution of glucose. But the result was negative.

14. In fine, acetylene, cyanogen, and arseniuretted hydrogen, that is to say, gases formed by the absorption of heat but which do not explode by simple heating, may be caused to explode under the influence of a sudden and very violent shock, such as that which results from the explosion of the mercury fulminate. This shock, in reality, only reaches a

[1] "Essai de Mécanique Chimique," tom. xi. p. 55.

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certain stratum of the gaseous molecules, to which it communicates an enormous energy. Under this shock the molecular edifice loses its relative stability, for which it was indebted to a special structure. Its interior connections having become broken, it crumbles, and the initial force becomes immediately strengthened by everything which answers to the heat of the decomposition of the gas. Hence a fresh shock, caused by the adjacent stratum, which also causes its decomposition, the actions co-ordinate themselves, reproduce and propagate one another, step by step, with similar characteristics, and in an extremely short interval of time, after the manner of the explosive wave, until the total destruction of the system is complete.

These are the phenomena which bring to light the direct thermo-dynamic relations existing between chemical and mechanical actions.

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CHAPTER VI.

EXPLOSIONS BY INFLUENCE.

§ 1. Experimental Observations.

1. So far we have studied the development of explosive reactions either from the point of view of their duration in a homogeneous system, all the parts of which are maintained at an identical temperature, or from their propagation in an equally homogeneous system which is fired directly by means of a body in ignition or by a violent shock. But the study of explosive substances has revealed the existence of another mode of propagating reactions in explosives; this propagation taking place at a distance and through the medium of the air or of solid bodies which of themselves do not participate in the chemical change.

We now refer to explosions by influence, which hitherto have been suspected from certain known facts in connection with the simultaneous explosion of several buildings, widely separated, in catastrophes at powder works.

Attention has been especially called to this class of phenomena by the study of nitroglycerin and gun-cotton.

2. We will first cite some characteristic facts.

A dynamite cartridge exploded by means of a priming of fulminate causes the explosion of cartridges in its vicinity, not only by contact and by direct shock, but even at a distance. An indefinite number of cartridges in a straight line or regular curve can also be exploded in this way.

The distances at which explosion will propagate itself are, comparatively speaking, considerable. Thus, for instance, with cartridges contained in stiff metallic cases, and placed on firm ground, the explosion caused by 100 grms. of Vonges dynamite (75% of nitroglycerin, 25% of randanite, that is to say of silica in a very finely divided state), communicates itself to a distance of 0·3 metre, according to Captain Coville's tests. D being the distance in metres and C the weight of the charge in kgms., the tests of this officer have given $D = 3{\cdot}0\,C$.

With cartridges resting on a rail he obtained $D = 7{\cdot}0\,C$.

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On a loose or free soil the distances were less. When the cartridge was suspended in the air, detonation did not take place by influence, probably because the cartridge not being fixed could easily recoil, thus diminishing the violence of the shock.

However, there are trials on record which show that air is sufficient to transmit detonation by influence, although less easily, and when dealing with large masses.

With dynamite containing less nitroglycerin (55% of nitroglycerin, and 45% of Boghead ashes) placed in cartridges of a similar nature and laid on the ground, the trials made by Captain Pamard gave shorter distances: D = 0·9 C.

If metallic casings having less resistance be used, the distance to which the explosion propagates itself is similarly reduced.

Dynamite when merely spread about on the ground even ceases to propagate the explosion.

Experiments made in Austria have given similar results. They have shown that the explosion communicates itself both in the open air with intervals of 0·04 metre and through deal planks 0·018 metre thick. In a leaden tube, with a diameter equal to 0·15 metre and 1 metre long, a cartridge placed at one extremity will cause the explosion of another cartridge placed at the opposite end.

The transmission of the explosion is more easily effected in tubes of cast iron. Joints lessen the susceptibility of transmission.

3. The explosion thus propagated may grow weaker from one cartridge to another and even change its character. Thus according to experiments made by Captain Muntz at Versailles in 1872, a first charge of dynamite when exploding direct had made a crater in the ground the radius of which was 0·30 metre. The second charge, which exploded by influence, produced a hollow merely of 0·22 metre; the effect of the detonation had therefore become lessened. This diminution should become manifest particularly towards the limit of the distances at which the influence ceases.

In the same way four tinplate screens were placed at intervals of 0·040 metre, and a small cylinder of gun-cotton was placed against each of them, the whole fixed on a board. At a distance of 0·015 metre in front of the first screen, a similar cylinder was exploded. All the cylinders exploded, but a progressive diminution was observed in the cavities produced in the board placed below each cylinder.

According to these facts, propagation by influence depends both on the pressure acquired by the gases and on the nature of the support. It is not even necessary that this support should be firm.

It has been ascertained that these effects are not generally due to simple projections of fragments of casing or of the neigh-

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bouring substances, although such projections often play a certain part. In this respect, the real character of the effects produced is shown more particularly from tests made under water.

4. In fact, when experimenting in water, below a depth of 1·30 metres a charge of dynamite weighing 5 kgms. will cause the explosion of a charge of 4 kgms. situated at a distance of 3 metres.

The water therefore transmits the explosive shock, at any rate to a certain distance, in the same way as a solid body. This transmission is so violent that fishes are killed in ponds within a certain radius by the explosion of a dynamite cartridge; this process is sometimes employed by fishermen, but has the disadvantage of destroying all the fish.

5. Similar trials have been made by Abel with compressed gun-cotton. According to his observations the explosion of a first block determines the explosion of a series of similar blocks. This propagation has also been studied under water; the explosion of a torpedo charged with gun-cotton causing the explosion of neighbouring torpedoes placed within a certain radius.

Sudden pressures transmitted by water have even been measured by the aid of the lead crusher at different distances, such as 2·50 metres, 3·50 metres, 4·50 metres and 5·50 metres. They decrease with the distance, as might be expected. Besides, experience proves that the relative position of the charge and the crusher is immaterial, and this is in accordance with the principle of equal transmission of hydraulic pressures in all directions.

6. Explosions of fulminating substances, propagating themselves suddenly to a great number of amorces, belong to the same order of explosions by influence.

The explosion in the Rue Beranger has been previously mentioned (p. 46). The experiments made on that occasion by Sarrau showed that amorces, similar to those which caused this catastrophe, will burn successively by simple inflammation during a fire without giving rise to a general explosion, whereas the explosions of some of these amorces each containing 0·010 grm. of explosive matter, if produced by a sudden pressure, determines, by influence, the explosions of neighbouring packets even when not contiguous, and when situated at a distance of 0·15 metre. A general explosion, therefore, can be easily produced by influence under these conditions.

§ 2. Theory founded on the Existence of the Explosive Wave.

1. It follows from these facts, and particularly from experiments made under water, that explosions by influence are not due to inflammation, properly so called, but to the transmission

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of a shock resulting from enormous and sudden pressures produced by nitroglycerin or gun-cotton, the energy of which shock is transformed into heat in the explosive substance (see pp. 36, 57).

2. In an extremely rapid reaction, the pressure may approach the limit corresponding to the matter exploding in its own volume; and the disturbance due to the sudden development of pressures, nearly theoretical, may propagate itself either by the mediation of the ground and of the supports, or through the air itself, when projected *en masse*, as has been shown by the explosions of certain powder mills, gun-cotton magazines, and also by some of the experiments made with dynamite and compressed gun-cotton. The intensity of the shock propagated either by a column of air or by a liquid or solid mass, varies according to the nature of the explosive body and its mode of inflammation; it is more violent the shorter the duration of the chemical reaction and the more gas there is developed; that is to say, a stronger initial pressure and a greater heat, or, in other words, greater work for an equal weight of explosive substance (see pp. 40, 41).

3. This transmission of the shock is more easily effected by solids than by liquids, and more easily by liquids than by gases; in the case of gases it takes place all the more easily if they are compressed. It is propagated all the more easily through solids when these are hard; iron transmits better than earth, and hard earth better than soft soil.

Any kind of junction has a tendency to weaken, especially if any softer substance intervene. Hence the employment as a receptacle of a tube formed of a goose quill, will stop the effect of mercury fulminate, whereas a copper tube or capsule transmits this effect in all its intensity.

Explosions by influence propagate themselves all the more easily in a series of cartridges, if the casing of the first detonating cartridge is very strong; this allows the gases to attain a very high pressure before the bursting of the casing (p. 40).

The existence of an air-space between the fulminate and the dynamite, will, on the other hand, diminish the violence of the shock transmitted, and consequently that of the explosion. As a general rule, the effect of shattering powders is lessened when there is no contact.

4. In order to form a complete idea of the transmission by supports of sudden pressures which give rise to shock, it is well to bear in mind the general principle whereby pressures in a homogeneous mass transmit themselves equally in all directions, and are the same over a small surface, whatever may be the direction. The explosions produced under water with gun-cotton show, as has been said above, that this principle is equally applicable to sudden pressures produced by explosive phenomena.

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But this ceases to be true when passing from one medium to another.

5. If the chemically inactive substance which transmits the explosive movement be fixed in a given position on the ground or on a rail on which the first cartridge has been placed, or again, held by the pressure of a mass of deep water, in which the first detonation has been produced, the propagation of the movement in this matter could scarcely have taken place except under the form of a wave of a purely physical order, a wave, the character of which is essentially different to the first wave which was present at the explosion, the latter being both of a chemical and physical order, and having been developed in the explosive body itself. While the first or chemical wave propagates itself with a constant intensity, the second, or physical wave, transmits the vibration starting from the explosive centre, and all around it, with an intensity which diminishes in inverse ratio to the square of the distance. In the immediate neighbourhood of the centre, the displacement of molecules may break the cohesion of the mass, and disperse it, or crush it by enlarging the chamber of explosion, if the experiment be carried out in a cavity. But at a very short distance, and the greatness of this depends on the elasticity of the surrounding medium, these movements, confused at first, regulate themselves, so as to give rise to the wave properly so called, characterised by sudden compressions and deformations of the substance. The amplitude of these undulatory oscillations depends on the greatness of the initial impulse.

They progress with an excessive rapidity, at the same time constantly decreasing in intensity, and they maintain their regularity up to points at which the medium is interrupted. There these sudden compressions and deformations change their nature, and transform themselves into an impelling movement, that is to say, they reproduce the shock. If then they act on a fresh cartridge they will cause it to explode. This shock will further be attenuated by distance, owing to the decrease thus introduced into its intensity. Consequently the character of the explosion may be modified. The effects will thus diminish up to a certain distance from the point of origin, beyond which distance the explosion will cease to produce itself.

When the explosion has taken place in a second cartridge the same series of effects is reproduced from the second to the third cartridge, but they depend upon the character of the explosion in the second cartridge and so on.

6. Such is the theory which appears to the author to account for explosions by influence, and for the phenomena which accompanies them. It rests on the production of two orders of waves, the one being the explosive wave, properly so called, developed in the substance which explodes, and consisting of a

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transformation incessantly reproduced from chemical actions into calorific and mechanical actions, which transmit the shock to the supports and to contiguous bodies; and the other purely physical and mechanical, which also transmits sudden pressures around the centre of vibration to neighbouring bodies and by a peculiar circumstance to a fresh mass of explosive matter.

The explosive wave, once produced, propagates itself without diminishing in force, because the chemical reactions which develop it regenerate its energy proportionately along the whole course; whereas the mechanical wave is constantly losing its intensity in proportion as its energy, which is determined only by the original impulsion, is distributed into a more considerable mass of matter.

7. A different theory than this was at first proposed by Abel, namely, the theory of *synchronous vibrations*, of which it will be well to speak now. According to this authority the determining cause of the detonation of an explosive body resides in the synchronism between the vibrations produced by the body which provokes the detonation and those which would be produced by the first body when detonating, precisely as a violin-string resounds at a distance in unison with another chord, set in vibration. In support of this, Abel cited the following facts. In the first place, detonators appear to be special for each kind of explosive substance. For instance, nitrogen iodide, which is very susceptible to shock and friction, does not appear to be able to cause the detonation of compressed gun-cotton. Nitrogen chloride, so easily explosive of itself, only produces detonation when a weight ten times that of the necessary fulminate is employed. In the same way nitroglycerin does not cause the detonation of gun-cotton in sheets on which the envelope containing it is placed. In this way 23·3 grms. of nitroglycerin have been made to detonate without success. On the other hand, the inverse influence is proved, 7·75 grms. of compressed gun-cotton having detonated nitroglycerin enclosed in an envelope of thin foil at a distance of 0·02 metre. A priming formed of a mixture of potassium ferrocyanide and potassium chlorate will not cause gun-cotton to detonate (according to Brown).

Finally, according to Trauzl, a much greater weight of a priming made of a mixture of mercury fulminate and potassium chlorate should be taken than if it were formed of fulminate alone. Nevertheless the heat liberated by unit weight is one-fifth greater with the former mixture.

8. Champion and Pellet have adduced the following experiments in support of this ingenious hypothesis: they fixed on the string of a contra-bass particles of nitrogen iodide, a substance which detonates by the slightest friction. They then caused the strings of a similar instrument situated at a

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distance to vibrate; detonation took place, but only for sounds higher than a given note, which note represented sixty vibrations per second. They then took two conjugate parabolic mirrors fixed 2·5 metres apart, and they placed along the line of foci at different points a few drops of nitroglycerin or grains of nitrogen iodide, then they caused the detonation of a large drop of nitroglycerin on one of the foci; they observed that the explosive substances placed on the conjugate focus exploded in unison, to the exclusion of similar substances placed at other points. A coating of lamp-black placed on the surface of mirrors served to prevent any reflection and the concentration of the calorific rays.

9. None of these tests, however, are conclusive, and several of them appear absolutely contrary to the theory of synchronous vibrations. In the first place it may be remarked that the fact of a certain musical note being capable of determining each kind of explosion has never been established properly; it is only below a certain note that the effects cease to be produced, whereas they take place by preference, and whatever be the explosive body, in the sharpest notes. Besides, the effects cease to be produced at distances incomparably less than the resonance of the chords in unison, which proves that detonations are functions of the intensity of mechanical action rather than of the character of the vibration which determines them. Detonation also ceases to be produced when the weight of the detonator is too slight, and consequently when the energy of the shock is attenuated. The specific vibrating note, however, which determines explosion should always remain the same. For instance, cartridges of 75 per cent. dynamite cease to explode when the capsule contains less than 0·2 grm. of fulminate; the explosion only being insured in any case at the regulation weight of 1 grm. This confirms the existence of a direct relation between the character of the detonation and the intensity of the shock produced by one and the same detonator.

If it were true that gun-cotton could explode nitroglycerin by reason of the synchronism of the vibration transmitted, it is difficult to understand why reciprocal action does not take place; whereas the absence of reciprocity is easily explained by the difference in the structure of the two substances, which plays an important part in the transformation of energy into work (p. 38).

10. This same diversity of structure and the modifications which it introduces into the transmission of the phenomena of shock, and the transformation of mechanical energy into calorific energy, may be quoted in order to account for the facts observed by Abel.

The difference between the energy of pure fulminate and that of fulminate when mixed with potassium chlorate is not any

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less easy to explain; the shock produced by the former body being more sudden by reason of the absence of all dissociation of the product, which is no other than carbonic oxide; this absence should be opposed to the dissociation of carbonic acid which is produced in the second case. Probably also the formation of potassium chloride disseminated in the gases produced with the aid of potassium chlorate serves to attenuate the shock, like the silica in dynamite.

11. All the effects observed with nitrogen iodide are explained by the vibration of the supports, and by the effects of the resulting friction, this substance being eminently susceptible to friction.

12. The experiment with the conjugate mirrors is accounted for quite as fairly by the concentration of movements of the air in the focus, and consequently by the mechanical effects resulting therefrom.

13. Lambert has further shown in experiments carried out on behalf of the *Commission des substances explosives* that in the case of the explosion of dynamite cartridges when produced in cast-iron tubes of large diameter, there did not appear to be any difference as far as regards detonations caused by influence between the nodal and internodal parts of the tube.

14. Being anxious to clear up the question altogether, by eliminating the influence of the supports and the diversity of cohesion and of the physical structure of solid explosive substances, the author has undertaken special tests on the chemical stability of matter in sonorous vibration. A summary of the result will now be given.

§ 3. Chemical Stability of Matter in Sonorous Vibration.

1. A large number of chemical transformations are now attributed to the energy of ethereal matter, animated by these vibratory and other movements which produce calorific, luminous, and electric phenomena. This energy, when communicated to ponderable matter, produces therein decompositions and combinations. Is it the same with the ordinary vibrations of ponderable matter—that is to say, with sonorous vibrations which are transmitted according to the laws of acoustics? The question is a very interesting one, and touches especially on the study of explosive substances.

The ingenious experiments above recorded have been published by Noble and Abel, as well as by Champion and Pellett, and many authorities admit that explosive bodies may detonate under the influence of certain musical notes, which would cause them to vibrate in unison. However seductive the theory may be, the results obtained so far do not, however, establish it beyond dispute. Explosions of dynamite and gun-cotton by

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influence are explained more simply, as has been said above, by the direct effect of the shock propagated by gases at short distances, beyond which they do not propagate themselves in any way. As to nitrogen iodide, which is the subject of the

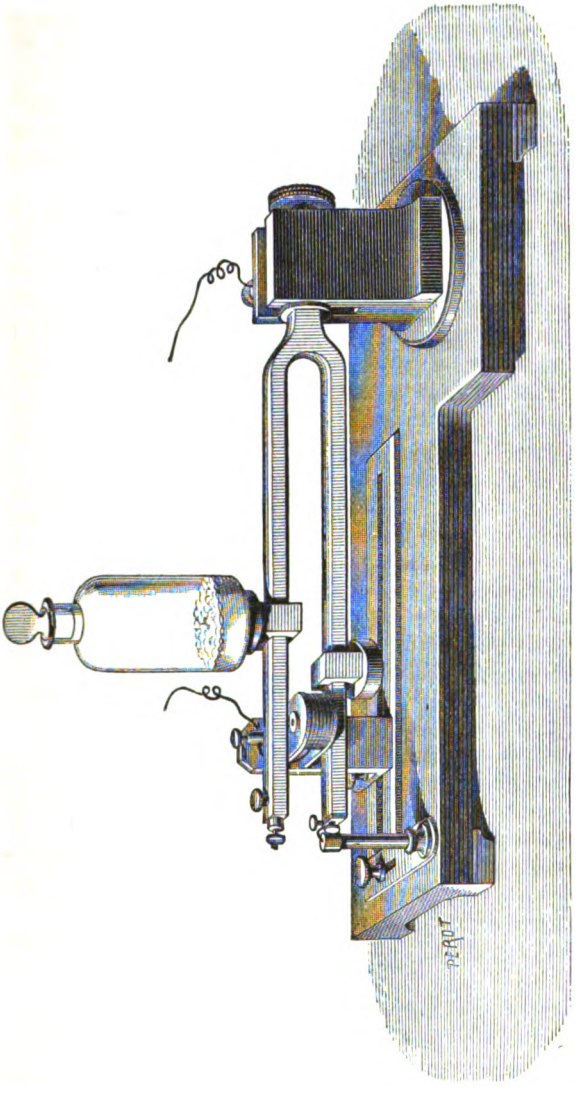

Fig. 7.

principal observations relative to explosions by resonance, it is a powder so sensitive to friction that it may be asked whether its detonation does not take place by shock and by the friction of the supports, the real seat of resonance in unison.

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2. The author deemed it expedient to make fresh researches with gases and with liquids, which substances are more suitable for propagating the vibratory movement, properly so called, than a powder. Substances were selected decomposable with liberation of heat, so as to lessen the importance of the part played by the vibratory movement, in propagating reaction without compelling it to do all its work in virtue of its own energy. Finally, experiments were made on unstable bodies, and even during a state of continuous decomposition which it was merely a question of accelerating: these apparently are the most favourable conditions. The whole question was to make the substance resound into chemical transformation. The trials were carried out by two processes which correspond to vibrations of very unequal rapidity, namely:—

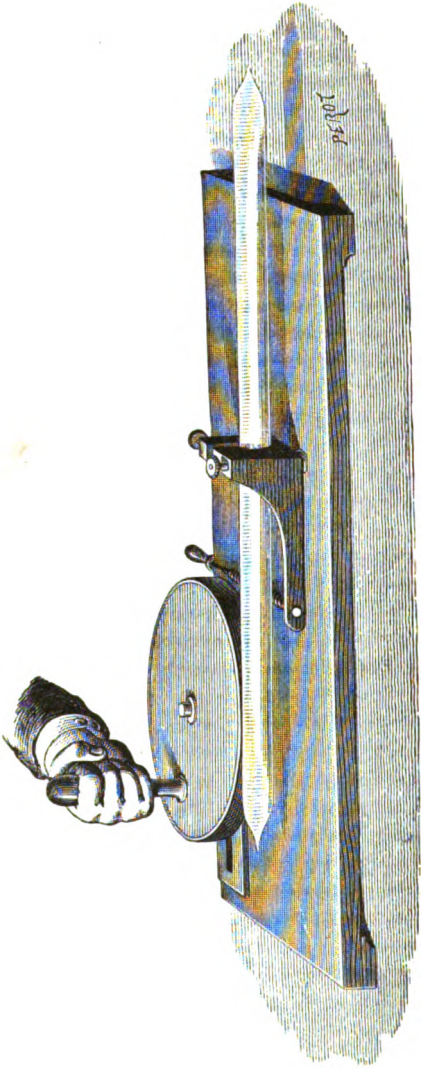

Fig. 8.

1st. By means of a large horizontal tuning fork moved by an electric interruptor, and one of the arms of which was loaded with a bottle of 250 cms. capacity, containing the gas or liquid, the other arm bearing an equivalent weight. The effective vibration of the bottle has been verified, as also that of the liquid, otherwise manifested by ordinary optical appearances. This arrangement has supplied about 100 simple vibrations per second (Fig. 7).

2nd. By means of a large horizontal glass tube sealed at both

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ends, holding about 400 c.c., 60 cms. long and 3 cms. wide, placed in longitudinal vibration by the friction of a horizontal wheel provided with a moist piece of felt. This very simple appliance, which Koenig has arranged, produced, during experiments on ozone, 7200 simple vibrations per second, according to observations taken by this expert (Fig. 8).

The sharpness of this note is almost intolerable.

The following are the results observed with ozone, arseniuretted hydrogen, and sulphuric acid in the presence of ethylene, oxygenated water, and persulphuric acid.

3. *Ozone.*—The oxygen used contained such proportions of ozone as 58 mgrms. per litre, a degree easily obtainable with the author's appliances. With the tuning fork (100 vibrations), a state of vibration having been maintained for an hour and a half, the amount of ozone in the gas remained constant, both with dry ozone and with ozone mixed with 10 c.c. of water. This latter did not either lower the degree of the ozone or supply oxygenated water.[1]

With the tube and wheel (7200 vibrations), the state of vibration being maintained for half an hour, the degree of dry gas did not vary. The absorption of the ozone was determined subsequently by standard solution of arsenious acid: the diminution in the strength of the latter was found equivalent to 171 div. of permanganate; while this diminution was precisely 171 in an equal volume of the same gas analysed previous to the test.

Now, ozone is a gas which is transformed into ordinary oxygen with liberation of heat (— 14,800 cal. for Oz. = 24 grms.), and it became transformed spontaneously in a slow and continuous manner, passing from 53 mgrms. to 29 mgrms. in 24 hours, when it was left to itself in the conditions above given. Nevertheless, it may be seen that its transformation was not accelerated by a movement which caused it to vibrate 7200 times per second for half an hour. Its spontaneous decomposition could not therefore be attributed to these sonorous vibrations which constantly traverse all bodies in nature.

Such an absence of reaction is not, on the other hand, explicable by an inverse influence, for a similar tube filled with pure oxygen did not modify the strength of the arsenious solution after similar vibration and for a similar space of time.

4. *Arseniuretted Hydrogen.*—A similar vibratory movement communicated to a tube filled with this gas, and afterwards sealed, did not modify it; nevertheless, in the space of 24 hours, the tube began to be covered with a coating of metallic

[1] In these experiments it will be well to guard against the alkalinity of glass, which will rapidly destroy the ozone. When using pulverised glass one is specially exposed to this accident.

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arsenic, as a tube does which is filled with the same gas and which has not undergone any vibration. This gas reduces itself into its elements, liberating, according to Ogier, + 36,700 cal., which explains its instability. We see, therefore, that it is not increased by the sonorous vibrations.

5. *Ethylene and Sulphuric Acid.*—The author endeavoured to accelerate the slow combination of these two bodies, which is so easily effected under the influence of continuous agitation and by the concurrence of shocks produced by a mass of mercury, by having recourse to the vibratory movement. This slow combination is exothermal.

A bottle of 240 c.c. containing pure ethylene, and also 5 c.c. to 6 c.c. of sulphuric acid and mercury, has been set in vibration by a tuning fork (100 vibrations per second); the acid vibrated and was pulverised on the surface; yet at the end of half an hour the absorption of gas was slight, and very nearly the same as in a similar bottle kept immovable in a distant room.

6. *Oxygenated Water.*—10 cc. of a solution containing 9·3 mgrms. of active oxygen, placed in a bottle of 250 c.c. capacity, are not altered in degree by the effect of the movement of the tuning fork (100 vibrations per second) kept up for half an hour. Yet the liquid actually vibrated and lost 0·9 mgrms. of oxygen every 24 hours; 10 c.c. of a solution containing 6·3 mgrms. of active oxygen set in vibration (7200 vibrations) in a tube of 4 c.c. full of air for half an hour gave afterwards 6·25 mgrms.

7. *Persulphuric Acid.*—Same results with the tuning fork (100 vibrations); initial degree 13 mgrms., final degree 12·6 mgrms. With the tube (7200 vibrations), initial degree 3·6 mgrms., final degree 2·8 mgrms. The difference here appears slightly to exceed the rapidity of spontaneous decomposition, this rapidity being greater than with oxygenated water, but it scarcely ever exceeds the limit of error.

The results observed with these liquids merit all the more attention since it has been possible to assimilate these systems *à priori* to the liquids containing oxygen in a state of supersaturated solution, a solution which agitation, and particularly a vibratory movement, will reduce to its normal state. In fact, the foregoing liquids will certainly hold a certain quantity of oxygen in this state, as may be easily proved; but this amount of oxygen does not act either on the permanganate or on the potassium iodide employed, and it should be studied apart. As a matter of fact, it does not intervene here in any equilibrium of dissociation capable of being influenced by the separation of the oxygen and the oxygenated water. It would doubtless be otherwise in a system in a state of dissociation, and the equilibrium of which would be maintained by the presence of a gas actually dissolved; but then it would no longer be a question

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of a direct influence of the vibratory movement on chemical transformation. The tests made with gases such as ozone and arseniuretted hydrogen are not subject to this complication; they tend to do away with the hypothesis of a direct influence of sonorous vibrations, even when very rapid, of the gaseous particles on their chemical transformation.

8. It has been said that there is among the incessant and reciprocal shocks of gaseous particles, when in motion in an enclosed space, a certain number which are susceptible of raising the particles which undergo them to very high temperatures. If it were really so, a mixture of oxygen and hydrogen elements, which combine towards 6500°, would become gradually transformed into water, ammonia gas, decomposable at about 800°, would slowly change into nitrogen and hydrogen, etc. The author never observed anything like this in these gaseous systems preserved for a period of ten years. If this effect does not take place, it is probably due to the loss of energy in each gaseous particle regarded individually, and even its total energy remains comprised within certain limits.

9. In fine, matter is stable under the influence of sonorous vibrations, whereas it transforms itself under the influence of ethereal vibrations. This diversity in the mode of action of two kinds of vibrations is not surprising if we consider to what extent the sharpest sonorous vibrations are incomparably slower than luminous or calorific vibrations.

10. Yet there appears little doubt that the propagation of explosion by influence is caused by virtue of an undulatory movement; a complex movement of a chemical and physical order in the explosive substance which is transformed, whereas it is purely physical in intermediate substances whose nature is not changed. What also distinguishes this kind of movement from sonorous vibrations, properly so called, is the extreme intensity, that is to say, the greatness of the energy which it transmits. It is thus that the explosive wave propagates itself in the substance which explodes, not by reason of a single shock, the energy of which would become weaker as it propagates itself, but by reason of a series of similar shocks incessantly reproduced, and which, as they continue, regenerate the energy throughout the wave. On the other hand the propagation by air or by supports is effected solely by reason of the energy of the last shock communicated by the explosive substance, an energy which is no longer regenerated and which rapidly weakens by distance.

The explosive substance does not detonate because it transmits the movement, but, on the contrary, because it stops it, and because it transforms its mechanical energy on the spot into calorific energy capable of suddenly raising the temperature of the substance up to a degree which causes its decomposition.

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CHAPTER VII.

THE EXPLOSIVE WAVE.

§ 1. General Characteristics.[1]

1. The study of the various modes of decomposition of explosive substances, and especially that of detonation as compared with combustion, and of explosions by influence, leads to the admission of the existence of a wave motion peculiar to and characteristic of explosive phenomena; this is the explosive wave. It will be more accurately and completely defined by showing how it is propagated in gaseous systems. The results of the experiments which the author undertook in conjunction with M. Vieille led to the examination of the rate of propagation of the explosion in gases, the physical constitution of which gives to these researches a peculiar theoretical interest. In the experiments the conditions of the phenomena, the pressure of the gases, their nature and relative proportion, and the form, dimensions and nature of the vessels in which they are contained, were varied. They confirmed the existence of a new kind of wave motion of a compound nature, *i.e.* produced by a certain concordance between the physical and chemical impulses in the matter undergoing transformation. The wave motion once produced is then propagated from layer to layer throughout the whole mass, in accordance with the successive impulses of the gaseous molecules brought to a more intense state of vibration by the heat given off in their combination and transformed with but very slight displacement of their original position. Similar phenomena may be developed in explosive solids and liquids.

Such effects are comparable to those of a sound wave, but with this important difference, that the sound wave is transmitted onwards by degrees with little active energy, a very small excess of pressure, and with a velocity which depends solely on the

[1] "Comptes Rendus des séances de l'Académie des Sciences," tom. xciii. p. 21; tom. xciv. pp. 101, 149, 822; tom. xcv. pp. 151 and 199.

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physical constitution of the vibrating medium, this velocity being the same for all kinds of vibrations. But, in the case of the explosive wave, it is the change of chemical constitution which is propagated communicating to the moving system enormous energy and considerable excess of pressure. The velocity of the explosive wave is also much greater than that of sound waves transmitted through the same medium.

The explosive phenomenon is not reproduced periodically, it gives rise to one single characteristic wave, whereas the phenomenon of sound is generated by a periodical succession of waves resembling one another.

The characteristics of this new wave are—

(1) It is propagated uniformly, as shown in the experiments made with oxyhydric, oxycarbonic, and oxycyanic mixtures, which were made successively in tubes of lead, gutta-percha and glass, with lengths varying from 40 to 30 and 20 metres.

It is certain that disturbances are produced near the extremities of the tubes. However, they do not extend far under the conditions of the experiments; in fact, the experiments made with the tube closed, open at either or both ends, gave the same velocity, which remained the same for a given length.

(2) The velocity of the explosive wave depends essentially on the nature of the explosive compound, and not on the composition of the tube containing it (lead, gutta-percha).

(3) The influence of the diameter of the tube on the velocity of the wave is not appreciable between diameters of 5 mms. and 15 mms. It is, however, manifest in a capillary tube, but the diminution, even in this extreme case (2390 metres instead of 2840 metres), is not excessive. In short, the velocity depends less and less on the diameter in proportion as the increase of the latter leaves more liberty to the individual movements of the gaseous particles and diminishes the friction against the sides of the tube.

These conclusions are in accordance with those of M. Regnault on the velocity of the sound wave in tubes.[1]

(4) The velocity of the explosive wave is independent of pressure, between the limits 1 and 3, as referred to the pressure of the atmosphere. This is a fundamental property, for it establishes the fact that the rate of propagation of the explosive wave is governed by the same general laws as the velocity of sound.

(5) The theoretical relation which exists between the velocity of the explosive wave and the chemical nature of the gas which transmits it is more difficult to establish, this velocity depending on the temperatures, and these not being the same in the combustion of two different systems.

The inequality of the temperatures results from the unequal

[1] "Mémoires de l'Académie des Sciences," tom. xxxvii. p. 456.

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magnitude of the quantities of heat; for instance, 68,200 cal. for $CO + O$; 59,000 cal. for $H_2 + O$, supposing the water to be in the gaseous form; it also results, for the same quantity of heat, from the inequality of the specific heats. The calculation of these temperatures remains doubtful, on account of dissociation and uncertainties surrounding the value of specific heats at high temperatures.

An idea of the theoretical relation that regulates the velocity of the explosive wave may be formed, however, if it be noted that the total energy of the gas, at the moment of explosion, depends on its initial temperature, and on the heat given off during the combination itself. These two data determine the absolute temperature of the system, which is in proportion to the energy of translation ($\frac{1}{2}mv^2$) of the gaseous molecules. That is to say, the excess of energy communicated to the molecules by the act of the chemical combination is simply the heat given off in the reaction; the pressure exercised by the molecules on the sides of the vessels is the immediate translation of it, according to the most recent theories.

Thus a point is reached where mechanical notions and thermal notions tend to intermingle.

To formulate this, the rate of translation of the molecules at the moment of combination is proportional, according to the relation of the energy, to the square root of the ratio of the absolute temperature T, to the density of the gas as compared with air, or, as M. Clausius expresses it,

$$\theta = 29{\cdot}354 \text{ metres } \sqrt{\frac{T}{\rho}}$$

In reality, the physical notion of the temperature T does not enter into this estimation of the velocity, and the formula simply expresses the fact that the translating energy of the molecules of the gaseous system produced by the reaction, and containing all the heat developed by the latter, is proportional to the energy of translation of the same gaseous system, containing only the heat which it retains at zero.

This formula has been verified, approximately at least, for a score of gaseous compounds, differing greatly in their composition (as described hereafter).

2. Thus it seems, that in the act of explosion, a certain number of gaseous molecules amongst those forming the portion that is first ignited, are hurled forward with the velocity corresponding to the maximum temperature developed by the chemical combination, the shock which they impart determines the propagation of this combination into the next section, and the movement is reproduced from section to section with a velocity if not identical with, at least comparable to, that of the molecules themselves.

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The transmission of the energy, under these conditions of extreme rapidity of action, is perhaps effected with greater facility between gaseous molecules of the same nature, in virtue of a kind of unison causing similar movements, than between the molecules of gas and the enclosing vessel.

The action is not the same, as will be shown, in cases where the system in ignition has time to lose a portion of its heat, which is communicated to foreign gases or to bodies in the vicinity not capable of undergoing the same chemical transformation.

§ 2. Experimental Arrangements.

1. The mode of procedure adopted in this study is very simple. It consists,

(1) In filling with a detonating mixture under a given pressure, a tube of great length (about 40 metres, Figs. 9 and 10).

(2) In effecting the ignition at one of the extremities, by means of an electric spark (Fig. 11).

(3) In interrupting, by means of the flame itself, two electric

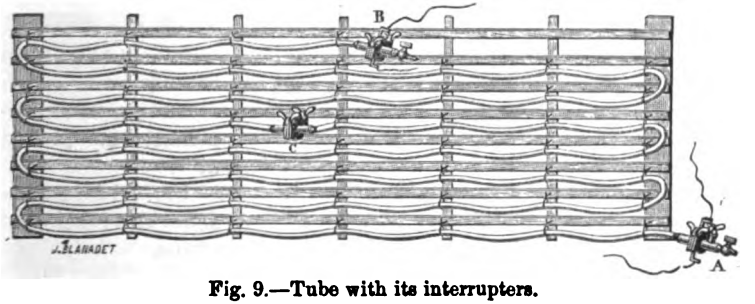

Fig. 9.—Tube with its interrupters.

currents, placed at certain points in the tube, the interval between which is exactly defined by two couplings which connect the consecutive portions of the tube (Figs. 13 and 14). The currents are transmitted along very narrow strips of tin (Fig. 12), gummed upon paper, and held by the couplings between the two insulating discs of leather, which have a hole in the centre, so as to establish the complete continuity of the bore. These strips are arranged normally to the direction of the flame.

A grain (about ·010 of a gramme) of mercury fulminate exploding on contact with the flame, destroys the strip and interrupts the current.

Potassium picrate has also been used to produce the same effect.

The gaseous compound is ignited by means of an electric spark, either at the beginning of the tube or at some given point.

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2. These arrangements will now be described in detail.

The tube has sometimes been laid in a single horizontal straight line, and sometimes in a succession of parallel rows, as shown in Fig. 9. The tube is represented as fixed upon a vertical wooden frame. It is provided with two terminal taps, A and B, and an intermediate interrupter, C.

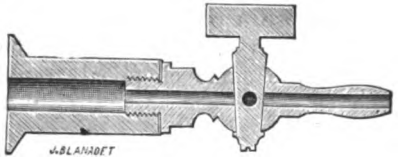

Fig. 10.—Terminal Tap.

Fig. 10 represents one of the terminal taps without any additional mechanism.

Fig. 11 represents a tap with a lateral tube enclosing an insulated metallic wire.

The spark is made to flash between the wire and the metallic casing of this pipe.

Fig. 12 shows the arrangement of one of the strips to be broken by the explosion; *s s* is the strip of tin, *p p* is the slip of paper on which the tin is glued.

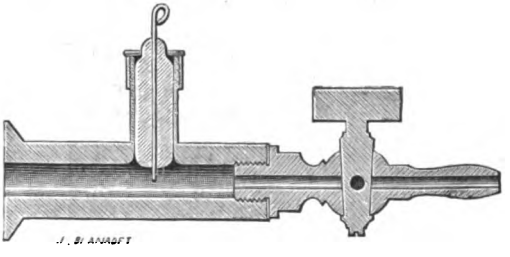

Fig. 11.—Tap and Apparatus for igniting by Electricity.

The tin is exposed at the point V of the tube T, which is shown in section.

The grain of fulminate is placed at *i*.

Fig. 13 represents the section of the coupling at right angles to the axis of the tube.

The coupling is marked C C C C. It is formed of four semicircular pieces facing each other in pairs, two only being shown in the figure; they are clamped together and round the tube T, by means of the screws E E.

Fig. 14 represents a section following the axis of the tube.

The tube T T T T shown in this figure is not the tube of gutta-percha itself, but a brass tube of the same section, on which the gutta-percha tube is fitted, either on one side only, or on both sides at once, as in Fig. 9. This arrangement is necessary for clamping the coupling and fixing the interrupters.

C C C C are the four parts of the coupling, the screws not being shown in order not to complicate the figure. The channel, V V, serves for the passage of the gas.

The strip of tin, *s s*, is held in position by small metallic supports, *r r*, on which the wires conveying the electric current are fixed.

Between the portions of the coupling, C C, are the two discs

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of insulating leather, shown here only in section, their projection being given in Fig. 12 (see letter T).

The grain of fulminate is always at *i*.

The time that elapsed between the two interruptions was estimated by means of the Le Boulengé chronograph, this instrument being capable of measuring to the $\frac{1}{20000}$ of a second.

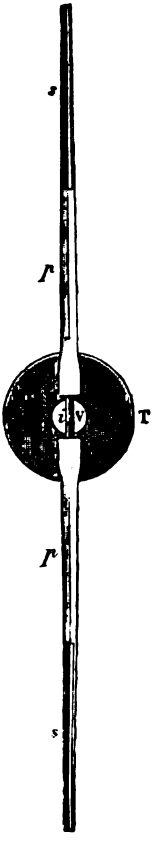

Fig. 12.—Strip of tin.

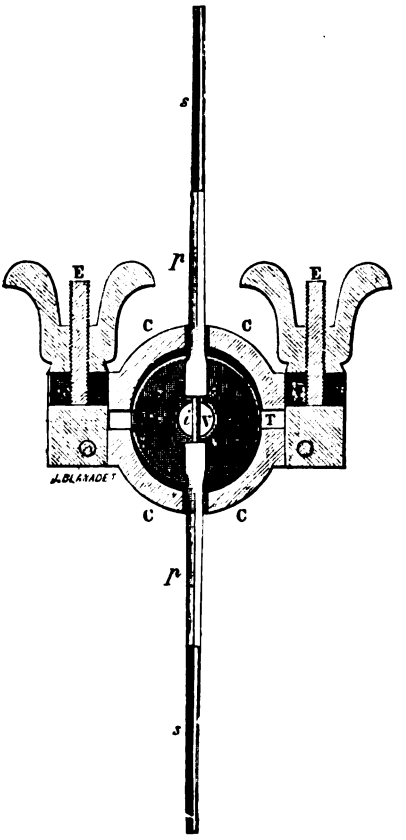

Fig. 13.—Coupling section at right angles to the axis of the tube.

The chronograph (Figs. 15 and 16) consists of two fundamental parts.

a. The *chronometer* T (Fig. 15), a long cylindrical rod suspended vertically, provided with zinc casing tubes, E, and held by magnetic attraction to the extremity of an electro-magnet, M, through which passes the first current destined to be broken.

b. The *registering apparatus*, T (Fig. 16), a similar cylinder

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held by the electro-magnet, M, through which passes the second current also destined to be interrupted.

A catch, C, consists of a knife edge (a circular milled head of hardened cast steel), mounted upon a spring which may be held firm, or tightened by the handle of a lever.

The chronometer, on its circuit being broken, becomes detached and falls vertically freely; the second circuit being next broken, the registering apparatus falls in its turn, comes in contact with the free extremity of the lever and disengages the catch, the knife is projected forward, strikes the chronometer in its course, and imprints upon its casing a mark, the position of which enables the rapidity of the phenomenon to be calculated. The details of this calculation, with corrections, will be found in the "Traité sur la poudre," etc., traduit et augmenté par Desortiaux, pp. 538 and 542. 1878 (Dunod).

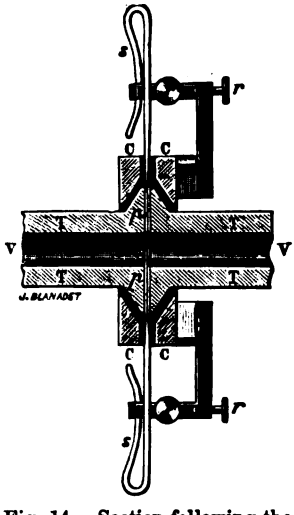

Fig. 14.—Section following the axis of the tube.

This method was found preferable to the registration by mechanical processes; the latter are subject to irregularities which are of great importance in such rapid phenomena.

The use of too short tubes for containing the gases was avoided, as this would exaggerate errors and expose the experiments to those well-known disturbances which arise in the vicinity of the source of the waves. Reference will be made to this point again, as it is one of great interest, and it will be shown at the same time that the variation in pressure of the gases is propagated with exactly the same rapidity as the ignition of the detonators.

§ 3. General Conditions of the Experiments.

Our experiments had reference,

1. To the arrangement of the tube;
2. To its composition;
3. To its characteristics, whether open or closed;
4. To its length;
5. To the initial pressure of the gaseous compound;
6. To the composition of this compound which was varied sometimes by introducing an inert gas, and sometimes by modifying the nature of the combustible gas.

Arrangement of the tube.—The first experiments were made

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with rectilinear and horizontal leaden tube 42·45 metres long [1] and ·005 of a metre in diameter.

It was filled with an electrolytic mixture of hydrogen and oxygen, under atmospheric pressure. After each experiment, the tube was dried by causing a current of dry air to circulate through it for several hours.

The following table gives all the experiments. The extreme results have not been eliminated from it as is sometimes done.

	Time observed in seconds.		Velocity per second.	
(1)	0·014633	...	2901·0	metres.
(2)	0·014597	...	2908·1	„
(3)	0·013914	...	3050·9	„
(4)	0·015047	...	2821·2	„
(5)	0·015816	...	2675·5	„
(6)	0·014752	...	2877·6	„
(7)	0·014782	...	2871·8	„
(8)	0·015253	...	2783·1	„
Mean	0·014860		2861·1	„

The mean variation in one experiment amounts to 79 metres, the maximum variation to + 190 metres and − 186 metres, corresponding to intervals of time equal to ± 0·00095, or at the maximum nearly $\frac{1}{1000}$ of a second, the mean error being half this quantity. With the oxyhydrogen mixture, the mean length measured on the rod of the chronographs is equal to ·0448 metre, which figures give a clearer idea of the degree of exactness attained in measurements of this order. With the mixture of carbonic oxide and oxygen, this length amounted to ·107 metre.

The mean error in the experiments is ten times as great as that recorded by the chronograph. This arises, not from the instrument itself, but from the unequal delays occurring in the process of interruption employed. It is known that such

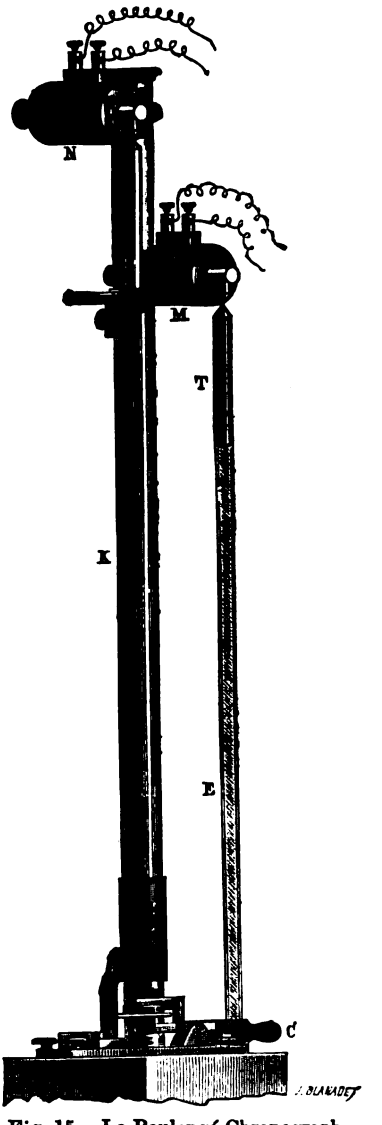

Fig. 15.—Le Boulengé Chronograph-chronometer.

[1] All the lengths are taken between the two interruptions.

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errors exist in all processes of this nature, and their magnitude must be estimated in each instance. In this case it amounted to 2·8 per cent. of the quantity measured, on an average, and to 6·6 in extreme cases.

Some trials made with a vertical tube, shorter it is true, gave the same velocities as with the horizontal tube.

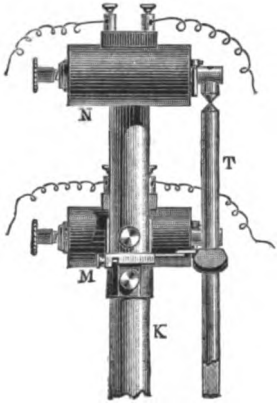

Fig. 16.—Le Boulengé Chronograph-registering apparatus.

The rectilinear arrangement of the tube such as was employed at first, required too extensive a space, and could only be effected in the open air and under conditions that were difficult to maintain and vary in prolonged experiments. For this reason the idea was conceived of laying the tube in the laboratory itself, in parallel horizontal rows separated by bends with a considerable radius of curvature; the whole was fixed upon a vertical frame (see Fig. 9, p. 91).

In this operation the length of the tube was increased by ·7 of a metre, bringing it to 43·135 metres.

The detonation was repeated under these new conditions, which gave for the velocity per second—

	Metres.
	2860·4
	2712·9
	2791·5
Average ...	2788·3

These figures are rather lower than in the preceding experiment, but they do not fall below the mean limits of error. It may therefore be assumed that the velocity is the same in the bent tube as in the straight one, and the general mean, 2841 metres, will be adopted.

Composition of the tube.—The unexpected magnitude of this velocity, which is intermediate between the velocity of sound in the detonating gaseous compound and in the metal constituting the tube, gave rise to some doubts. Was it really the rate of propagation of the detonation that was being measured, or was it not rather some particular vibratory movement propagated by the metal, arising from the explosion, produced at its extremity?

It seems, however, hardly probable that a propagation of this nature could cause the detonation of the fulminate, when we consider the weakness of the movement thus transmitted, and again the intervention of the leather discs T, between the metal

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and the strips of tin (Fig. 12). We may also mention the absence of detonation in certain grains of fulminate which had been slightly greased by accident, a circumstance which retarded the heating without otherwise modifying the explosive property. Again, when the flame is extinguished in its course, as we observed with the capillary glass tube, the furthest registering apparatus remains intact. We could not however feel assured on this point until we succeeded in reproducing our experiments and obtaining the same velocities in a tube of caoutchouc, a substance which could not be suspected of propagating the vibratory movement like metals. This was rendered possible by the fact that the internal combustion of the gaseous mixture is so rapid that it does not affect the material of which the tube is made. This caoutchouc tube was 40·109 metres long, and several mms. thick, its external diameter being 5 mms., and it was capable of supporting either a vacuum or an interior pressure of several atmospheres without any appreciable deformation. It was fixed upon the frame already described, in parallel lines (Fig. 9).

These were the results:—

	Velocity per second.
	2685 metres.
	2911 „
	2994 „
	2672 „
	2788 „
Mean ...	2810 „

This mean agrees with the value, 2841, obtained with the leaden tube, within the limits of error.

The propagation of the explosive phenomenon is thus independent of the composition of the tube, provided that the internal diameter remains the same.

We now come to some experiments made with a system of glass tubes, the total length of which was 43·24 metres, but the mean internal diameter only ·0015 metre. These were capillary tubes, each 2 metres in length, connected end to end by means of caoutchouc tubes, the whole being fixed upon the frame before mentioned (p. 91). The bends were made with the same glass tubing. We found—velocity per second, 2403 and 2279 metres; mean, 2341 metres.

These figures are rather lower than the foregoing ones, no doubt owing to the difference in the diameter; the propagation of the explosion being impeded in a capillary tube, as is the case also with the propagation of sound. The experiments made in glass enable us to see the propagation of the flame. Working in darkness, we see the entire length of the tube lighted up at the same moment, the eye not being able to perceive the progress of the flame.

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It sometimes happens that the flame does not reach the end of the tube, probably in consequence of the insufficient heating of the sections in advance of the mixture in ignition. One of the trials led to some important observations on this point. The flame being stopped in its course, without however going out, the aqueous vapour, condensed behind it, produced a backward draught upon the gas, and a return of the flame was observed very clearly towards its starting-point, this movement lasting during a very appreciable interval of time, a second, perhaps, for a distance of 2 metres. This shows well the difference between the progressive combustion of the gaseous compound and its detonation properly so called.

Diameter of the Tubes.—In order to investigate more fully the influence of the diameter of the tubes, it was thought advisable to make fresh measurements with a leaden tube, the internal diameter of which was equal to 15 mms., *i.e.* three times as great as the preceding one, and 30·43 metres long. Three experiments gave 2754, 2975, 3019 metres; mean, 2916 metres.

The experiments made with a leaden tube, the diameter of which was equal to 5 mms., having given 2841 metres, we see that the velocity is to all intents independent of the diameter of the tubes, reckoning from 5 mms.

It must be noted, however, that in a capillary glass tube (diameter 1·5 mms.), the velocity was found to be equal to 2341 metres, *i.e.* it was somewhat lower.

Closing of the Tube.—It may be asked is the rate of propagation of the detonation the same whether the tube be open or closed? It is only the latter case that strictly fulfils the conditions of combustion within a constant volume. To meet this question, experiments were made (with the caoutchouc tube), leaving open first the orifice farthest from the point of ignition; then the one nearest to this point; and, finally, both at once.

Three experiments of this nature gave—

	Velocity per second.
The farthest orifice only being open ...	2645 metres.
The nearest orifice only being open ...	3052 „
The two open together	2766 „
Mean ...	2821 „

The mean, with the same tube *entirely closed*, was 2810.

Thus the velocities have been found to be to all intents the same in all four cases. We see by this that the propagation of the detonation is so rapid that while it is taking place the gases are not projected forward, and have not time to escape from the tube to any appreciable extent—at least, in narrow tubes. This is explained by the fact that the detonation proceeds more

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rapidly than sound in the same gases, taken at the ordinary temperature. The condensation of the aqueous vapour, which is effected behind the flame, is also of little importance, since the time is too short to allow of its taking place to any appreciable extent.

Influence of the Detonators.—Do the minute detonators, employed for interrupting the electric current of the registering apparatus, help to regulate the propagation of the inflammation? In order to answer this question, it was sufficient to measure, not the time that elapsed between the destruction of two fulminate interrupters, placed at opposite extremities of the tube, but the interval between the breaking of the induction current of the coil that produced the spark at the beginning of the tube and the ignition of the fulminate interrupter placed at the farthest end of it.

The intervals of time observed, for a length of 40·054 metres, were—

·012556, ·012288, ·012904 secs.
Mean = ·012583 secs.

But there are errors in these figures, arising from delays in the registration, delays unequal in principle, as two different kinds of signals are involved. The difference between these two delays was calculated by measuring the time that elapsed between the signal of the spark and that of an interrupter ·05 metre away. This time is negative, *i.e.* the delay in the signal of the spark is greater than that in the signal of the interrupter. Three experiments gave—

·001559, ·001968, ·002129 sec.
Mean = ·001885 sec.

This correction, added to the above experiments, gives ·014468 secs., bringing the velocity to 2770 metres per second. The experiment made with two similar interrupters gave 2810 metres, the agreement of which result shows that the velocity observed is independent of the detonators.

This is still more clearly shown in some experiments hereafter described (p. 108), in which the propagation of the pressures had been registered by effecting the initial ignition by means of an electric spark. In fact, the propagation of the pressures starting a few centimetres from the beginning of the tube proceeds with a velocity of about 2700 metres, a rate in accordance with the results above mentioned.

Length of the Tube.—It now remained to ascertain whether the propagation of the explosion takes place uniformly in the tubes. This is clearly proved in the following experiments.

With the caoutchouc tube 5 mms. in diameter these results were obtained—

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Mixture ($H_2 + O$).

Distance of interrupters.	Velocity.	Mean.
40·109 metres	2810	
29·982 „ [1]	{2692 / 2716}	2704

Mixture ($CO + O$).

Distance of interrupters.	Velocity.			Mean.
Metres.	Metres.	Metres.	Metres.	Metres.
40·059 ...	1096 ...	1068 ...	1104 ...	1089
29·982[1] ...	1140 ...	1121 ...	— ...	1130
20·092[2] ...	1187 ...	1183 ...	— ...	1185

Again with the glass tube 1·5 mms. in diameter—

Mixture ($H_2 + O$).

Distance of interrupters.	Velocity.
43·340 metres [3]	2341 metres.
20·944 „	2433 „

In all these measurements, the differences between the velocities measured with unequal lengths do not exceed the limits of error.

Pressure.—The pressure was varied in the ratio of about 1 to 3. The caoutchouc tube (40·054 metres long) was employed, and with three different gaseous mixtures.

Mixture ($H_2 + O$).

Pressure (expressed by the height of a column of mercury).	Velocity.
0·560 metre	2763 metres.
0·760 „	2800 „
1·260 „	2776 „
1·580 „	2744 „

Mixture ($CO + O$).

Pressure.	Velocity.
0·570 metre	1120 metres.
0·760 „	1089 „
0·854 „	1072 „
1·560 „	{1140 / 1124} „
	1152 „

[1] A section of tubing 13 metres long filled with the same compound was afterwards added on; *i.e.* the interrupter was placed in the path of the flame, and not at the extremity of the tube.

[2] The interrupter was placed half-way along the tube, in the path of the flame.

[3] This time the interrupter was placed at the end of the tube.

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Mixture of cyanogen and oxygen ($CN + O_2$)

Pressure.					Velocity.	
0·388	metre	...	...	...	2171·4	metres.
0·758	„	...	...	{2224·7 / 2165·7}	2195·2	„
0·878	„	...	...	...	2052·4	„

Same conclusions.

Thus, as far as the experiments went, the rate of propagation of the detonation, either with the mixture of hydrogen and oxygen, or with the mixture of carbonic oxide and oxygen, is practically independent of the pressure, like the velocity of sound and the rate of translation of the gaseous molecules, which are analogous phenomena.

§ 4. Specific Velocity of the Explosive Wave.

1. We have now established the fact that the explosive wave is propagated uniformly and that its velocity is independent of the pressure, and also of the composition and diameter of the tubes, beyond a certain limit. Thus, this velocity constitutes for each inflammable compound, a true specific constant, the knowledge of which is of great interest, from the point of view of the theory of the movements of gases, and also from that of the employment of explosive substances. For this reason it was thought expedient to go more deeply into the study of this question, extending our operations to a large number of mixtures differing greatly in their composition.

2. Each experiment was repeated two or three times; it was generally performed in the caoutchouc tube, 40 metres long, with an internal diameter of 5 mms., and of great thickness (as already described, p. 97). The results obtained are shown in five tables, containing the most remarkable cases. In these tables, the first column gives the composition of the initial mixture; the second, the density of the products of combusition ρ, as compared with that of air, taken as unit; the third, the number, N, of molecular volumes of the elements (supposing them to be gaseous) entering into reaction, the volume being—

$$N\left[22{\cdot}32 \text{ litres} \times \frac{H}{760} \times (1 \times at)\right];$$

the fourth column gives the heat, Q, given off by the reaction, the water being supposed to be in a gaseous form[1]; the fifth column gives the square root of this quantity, $\sqrt{Q}$; the sixth contains the quotients $\frac{Q}{N \times 6{\cdot}8}$, 6·8 being the constant of the

[1] This quantity was measured near zero; but it would be little different at zero in the cases considered here, especially if the specific heat of the compound were estimated as the sum of the specific heats of its elements.

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specific heats of the elements under a constant pressure; this is the theoretical temperature, T, of the reaction; the seventh gives the theoretical values, θ, of the mean rate of translation per second of the gaseous molecules constituting the products of the combustion, a rate calculated for the temperature T, according to the formula of Clausius (see p. 90).

$$29{\cdot}354\sqrt{\frac{T}{\rho}}$$

This is a velocity which we propose to compare with the experimental velocity of the explosive wave, U, which is shown in the eighth column.

3. The temperature, T, is here calculated from the specific heats of the elements under a constant pressure. The results thus obtained, agree in general with the observations (columns 7 and 8); they agree far better than if the calculation were made from the specific heats at a constant volume, although the latter method would, on first thought, seem the more plausible.

We may account for the intervention of the specific heats under a constant pressure, if we consider that the combustion, in passing from layer to layer, is *preceded* by the previous compression of the layer of gas that it is about to transform. From that time the combustion takes place under a constant pressure throughout the tube. It might be thought that the temperature, T, must be increased by the elevation of temperature produced by this previous compression. But we must take into account the fact that the combustion of each layer produces, at the same time as heat, the work necessary for compressing the following layer; *i.e.* it loses in this way exactly the same quantity of heat as it has gained by its own compression. In short, as regards elevation of temperature, the effect is the same as if we were working under a constant pressure. The agreement between the figures calculated and the numbers observed confirms this view of the phenomena.[1]

The fact is, the physical conception of the temperature, T, does not enter into this estimate of the velocity, and the calculation simply shows that the energy of translation of the molecules of the gaseous system produced by the reaction, and

[1] It is assumed here that the specific heat of a compound gas under a constant pressure is the sum of the specific heats of its elements, which assumption is, in reality, only true when the volume is constant, or, for the two specific heats, in the case of gases formed without condensation. But this underestimate in the case of the specific heat under a constant pressure, of gases formed with condensation, is to a certain extent compensated by the fact that the specific heat of these gases rises with the temperature: this is proved by the study of the specific heats of carbonic acid, nitrogen monoxide, etc. ("Essai de Mécanique Chimique," tom. i. p. 440). This hypothesis may, therefore, be admitted for a first approximation.

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retaining all the heat thereby developed, is proportional to the energy of translation of the same gaseous system, containing only the heat that it retains at zero.

4. Here follow the series of tables :—

TABLE I.—ONE COMBUSTIBLE GAS ASSOCIATED WITH OXYGEN.

Nature of the mixture.	Density of the products. ρ	Number of molecular volumes of the elements. N	Heat of combustion (water gaseous). Q	$\sqrt{Q}$	$\frac{Q}{N \times 6{\cdot}8} = T$	Theoretical velocity. θ	Velocity found by experiment. U (per sec.).
			cal.		degrees.	metres.	metres.
Hydrogen . . . . $H_2 + O$	0·622	1·5	59,000	243	5780	2831	2810 (p. 97)
Carbonic Oxide . . $2CO + O_2$	1·529	1·5	68,200	261	6700	1941	1089 (p. 100)
Acetylene or Ethine . $C_2H_2 + O_5$	1·227	4·5	308,100	555	10,070	2660	$\left\{\begin{matrix}2525\\2440\end{matrix}\right\}$ 2482·5
Ethylene . . . . $C_2H_4 + O_6$	1·075	6·0	321,400	567	7880	2517	$\left\{\begin{matrix}2186·6\\2232·4\end{matrix}\right\}$ 2209·5
Ethane . . . . $C_2H_6 + O_7$	0·985	7·5	359,300	598	7050	2483	$\left\{\begin{matrix}2381·9\\2345·4\end{matrix}\right\}$ 2363
Methane . . . $2\,CH_4 + O_8$	0·924	4·5	193,500	440	6320	2427	$\left\{\begin{matrix}2313·2\\2260·0\end{matrix}\right\}$ 2287
Cyanogen . . . $CN + O_2$	1·343	4·0	262,500	512	9650	2490	2195 (p. 101)

According to the figures in this table, the theoretical velocity is very near the velocity found by experiment for hydrogen.

For the hydrocarbons and for cyanogen, this theoretical velocity is rather too high, the discrepancies being comprised between five and twelve hundredths, *i.e.* the formula keeps within an approximate value.

For carbonic oxide the discrepancy is much greater, exceeding forty hundredths; thus the formula is not applicable to this gas (see p. 107).

It will be seen that it remains approximate, even for gases that are formed with absorption of heat, and that give rise, upon their formation, to the highest temperatures of combustion, such as cyanogen and acetylene.

It is also approximate for very different ratios of volume between the combustible gases and the oxygen, such as 2 : 5, 6, 7, 8, in the series of the hydrocarbons, and 2 : 1 for the hydrogen.

Lastly, it is approximate for very unequal ratios of condensation in the combination, such as a condensation of a third (hydrogen), of a seventh (acetylene), or the absence of all condensation (ethylene, methane, cyanogen); or even an expansion (ethane). In the calculation of these volumes the water is

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assumed to be in the gaseous state in the hydrocarbons, a condition that does not enter into the case of carbonic oxide or cyanogen.

Thus it seems to be an established fact that the proposed formula represents approximately the velocity of the explosive wave for hydro-carbon gases.

5. This conclusion may be extended to the mixtures formed with these gases and hydrogen, or even carbonic oxide, as will be shown, the hydrogen imparting to these mixtures a law of detonation similar to its own.

TABLE II.—TWO COMBUSTIBLE GASES ASSOCIATED WITH OXYGEN.

Nature of the mixture.	Density of the products. ρ	Number of molecular volumes of the elements. N	Heat of combustion (water gaseous). Q	$\sqrt{Q}$	$\frac{Q}{N \times 6{\cdot}8} = T$	Theoretical velocity. θ	Velocity found by experiment. U (per sec.).
			cal.		degrees.	metres.	metres.
Carbonic oxide and hydrogen . . $CO + H_2 + O_2$	1·075	3	127,200	357	6230	2236	2008
$2CO + 3H_2 + O_5$	0·985	7·5	313,400	560	6150	2321	2096, 2245 } 2170
Ethylene and hydrogen . . . . $C_2H_4 + H_2 + O_7$	0·985	7·5	380,400	617	7460	2551	2411·4, 2422 } 2417
$C_2H_4 + 2H_2 + O_8$	0·924	9	439,400	663	7180	2588	2671, 2487·5 } 2579
Ethane and hydrogen $C_2H_6 + H_2 + O_8$	0·924	9	418,300	647	6830	2522	2184, 2227, 2339 } 2250 [1]

[1] Different preparations.

TABLE III.—ONE COMBUSTIBLE GAS ASSOCIATED WITH A COMPOUND COMBUSTIVE GAS.

Nature of the mixture.	Density of the products. ρ	Number of molecular volumes of the elements. N	Heat of combustion (water gaseous). Q	$\sqrt{Q}$	$\frac{Q}{N \times 6{\cdot}8} = T$	Theoretical velocity. θ	Velocity found by experiment. U (per sec.).
			cal.		degrees.	metres.	metres.
Nitrogen monoxide and hydrogen . $N_2O + H_2$	0·796	2·5	79,600	281	4680	2250	2254, 2314 } 2284
— and carbonic oxide $N_2O + CO$	1·250	2·5	88,800	298	5220	1897	1102·5, 1110·6 } 1106·5
— and cyanogen . $2N_2O + CN$	1·131	8	345,000	587	6340	2198	2035·5
Nitrogen dioxide and cyanogen . . $N_2O_2 + CN$	1·194	8	349,000	591	8550	2485	The detonation was not propagated in the tube.

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With the nitrogen monoxide, the velocity found by experiment is near the theoretical value for compounds containing hydrogen or cyanogen. With carbonic oxide we find the same anomaly as with oxygen.

6. One of the most interesting examples, and one most strongly confirming the theory, is the case of the isomeric compounds, *i.e.* those in which the composition of the final system is the same. In fact, in these cases the influence of the individual nature of the combustible gases, and even that of the combustive ones, is eliminated.

TABLE IV.—ISOMERIC MIXTURES.

Nature of the mixture.	Density of the products. ρ	Number of molecular volumes of the elements. N	Heat of combustion (water gaseous). Q	$\sqrt{Q}$	$\frac{Q}{N \times 6{\cdot}8} = T$	Theoretical velocity. θ	Velocity found by experiment. U (per sec.).
	First Group.—Hydro-Carbon Gases and pure Oxygen.						
	(1) Methane and Isomeric Mixtures.						
			cal.		degrees.	metres.	metres.
$2(CH_4 + O_4)$ . . .	0·924	9	387,000	622	6320	2427	2287
$C_2H_6 + H_2 + O_5$.	0·924	9	418,300	647	6830	2522	2250
$C_2H_4 + 2H_2 + O_5$.	0·924	9	439,400	663	7180	2588	2579
	(2) Ethane and Isomeric Mixtures.						
$C_2H_6 + O_7$ . . .	0·985	7·5	359,300	598	7050	2483	2363
$C_2H_4 + H_2 + O_7$.	0·985	7·5	380,400	617	7460	2551	2417
	Second Group.—Hydro-carbon Gases compared with Oxy-carbon Mixtures.						
	(3) Ethylene and Isomeric Mixtures.						
$C_2H_4 + O_6$ . . .	1·075	6	321,400	567	7880	2517	2219·5
$2(CO + H_2 + O_2)$.	1·075	6	254,400	504	6230	2236	2208
	(4) Ethane and Isomeric Mixtures.						
$C_2H_6 + O_7$ . . .	0·985	7·5	359,300	598	7050	2483	2363
$2CO + 3H_2 + O_5$.	0·985	7·5	313,400	560	6150	2321	2170
	(5) Cyanogen mixed with Nitrogen and Isomeric Mixtures.						
$2CN + N_2 + O_4$ . .	1·250	5	262,500	512	7720	2334	{2116·0 / 1971·2} 2043·6
$2(CO + N_2 + O)$.	1·250	5	136,400	370	4010	1661	1000 ?[1]
	Third Group.—Compound Oxygen yielding Gases, compared with Mixtures formed with pure Oxygen.						
	(6) Hydrogen.						
$H_2 + N_2O$ . . .	0·796	2·5	79,600	281	4680	2250	2284
$H_2 + N_2 + O$ . .	0·796	2·5	59,000	243	3470	1935	2121
	(7) Carbonic Oxide.						
$CO + N_2O$ . . .	1·250	2·5	88,800	298	5220	1897	1106·5
$CO + N_2 + O$ . .	1·250	2·5	68,200	261	4010	1661	1000 ?[1]

[1] The detonation is not usually propagated. However, this figure was found among the author's notes without other detail.

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These compounds satisfy the law fairly closely, with the exception of the carbonic oxide. The isomeric compounds have generally approximate velocities. They enable us to appreciate more exactly the influence of the heat given off, Q, eliminating that of the density, the specific heat of the products, and even of individual composition, which are the same.

Thus, in order to make a comparison, it is merely necessary to divide the velocities found by $\sqrt{Q}$.

Thus—

1st system	... 3·68	... 3·48	... 3·69
2nd „	... 3·95	... 3·92	
3rd „	... 3·91	... 3·98	
4th „	... 3·93	... 3·88	
5th „	... 3·99	... 2·70	
6th „	... 8·13	... 8·73	
7th „	... 3·67	... 3·83	

It will be seen in general the coincidence is still more marked, with the exception of the fifth system, in which carbonic oxide, which does not satisfy the general theory, is compared with cyanogen.

We will now examine the influence of inert gases, which do not participate in the chemical reaction.

TABLE V.—COMBUSTIBLE GASES, OXYGEN AND INERT GASES.

Nature of the mixture.	Density of the products. ρ	Number of molecular volumes of the elements. N	Heat of combustion (water gaseous). Q	$\sqrt{Q}$	$\frac{Q}{N \times 6 \cdot 8} = T$	Theoretical velocity. θ	Velocity found by experiment. U (per sec.)
			cal.		degrees.	metres.	metres.
Hydrogen and nitrogen							
$H_2 + O$	0·622	1·5	59,000	243	5780	2831	2810
$H_2 + N_2 + O$	0·796	2·5	59,000	243	3470	1935	2121
0·3H + 0·7 air	0·846	3·33	59,000	243	2610	1820	1439
0·267H + 0·733 air	0·868	3·80	59,000	243	2287	1505	1201
0·233H + 0·768 air	0·885	4·27	59,000	243	2042	1409	1205
0·217H + 0·783 air	0·895	4·56	59,000	243	1903	1389	The detonation was not propagated.
Carbonic oxide and nitrogen							
$CO + O$	1·529	1·5	68,200	261	6700	1941	1089
$CO + N_2 + O$	1·250	2·5	68,200	261	4010	1661	1000 ? Propagation doubtful.
0·3CO + 0·7 air	1·165	4·33	68,200	261	2260	1236	The detonation was not propagated.

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TABLE V.—COMBUSTIBLE GASES, OXYGEN AND INERT GASES—(*Continued*).

Nature of the mixture.	Density of the products. ρ	Number of molecular volumes of the elements. N	Heat of combustion (water gaseous). Q	$\sqrt{Q}$	$\frac{Q}{N \times 6 \cdot 8} = T$	Theoretical velocity. θ	Velocity found by experiment. U (per sec.).
			cal.		degrees.	metres.	metres.
Methane and nitrogen							
$CH_4 + O_4$	0·923	4·6	193,500	440	6320	2427	2287
$CH_4 + 2N_2 + O_4$	0·942	6·5	193,500	440	4378	2002	1858
$CH_4 + 4N_2 + O_4$	0·951	8·5	193,500	440	3347	1744	1151
$CH_4 + 7{\cdot}52N_2 + O_4$ methane and air	0·958	12·0	193,500	440	2371	1450	The detonation was not propagated.
Cyanogen and nitrogen							
$2CN + O_4$	1·343	4·0	262,500	512	9650	2490	2195
$2CN + N_2 + O_4$	1·250	5·0	262,500	512	7720	2334	2044
$2CN + 2N_2 + O_4$	1·194	6·0	262,500	512	6340	2152	1234·7, 1172·7 } 1203·3
$2CN + 4N_2 + O_4$	1·127	8·0	262,500	512	4825	1920	The detonation was not propagated.

Detonation was not effected in a mixture richer in nitrogen. The mixture $CO + N_2 + O$ is doubtful.

The general relations were the same, except for the compounds that border upon the limit at which the detonation ceases to be propagated, such as the mixture of cyanogen with twice its volume of nitrogen, that of methane with four times its volume of nitrogen, carbonic oxide, etc. With hydrogen and an excess of nitrogen, there was also a decided fall in the results.

7. To sum up, the velocity of translation of the gaseous molecules, preserving the whole of the energy corresponding to the heat given off by the reaction, may be regarded as a limit representing the maximum rate of propagation of the explosive wave.

But this velocity is diminished by the contact of gases and other foreign bodies; and also when the mass ignited at the beginning is too small and too rapidly cooled by radiation; and again when the elementary velocity of the chemical reaction[1] is too feeble, as seems to be the case with carbonic oxide. Under these conditions the wave slackens, and may even stop altogether, the combustion being then propagated from layer to layer at a much slower rate. Reference will be made to this point again.

[1] "Essai de Mécanique Chimique," tom. ii. p. 14.

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§ 5. On the Period of Variable Condition preceding Detonation and the Conditions of the Establishment of the Explosive Wave.

1. It is now proposed to study the conditions of the establishment of the explosive wave, and the period of variable condition preceding this establishment, a period analogous to that which precedes the establishment of the sound wave.

2. The following process has enabled precise measurements to be made of the variation of the velocities during very short intervals of time, such as ·0003 of a second.

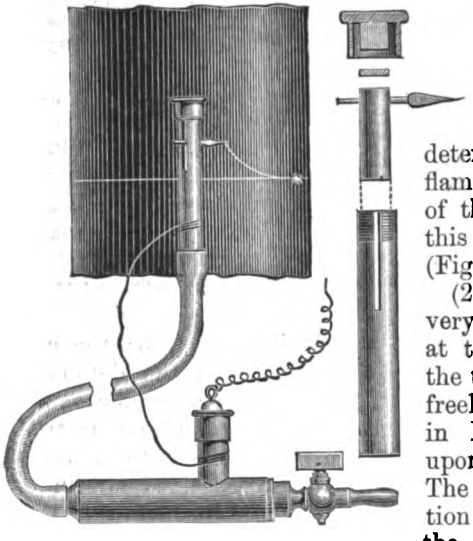

Fig. 17.—Registration of variable velocities.

A revolving cylinder gives the following record:

(1) The spark that determines the initial inflammation at the mouth of the tube; the trace of this spark is shown at *e* (Fig. 18).

(2) The movement of a very light piston, placed at the other extremity of the tube, in which it moves freely. This piston is shown in Fig. 17 in projection upon the revolving cylinder. The details of its construction are here shown: *i.e.* the tube, the piston furnished with its pencil intended to trace its course upon the cylinder, and lastly the terminal cap of the piston tube.

In this way is recorded the time that elapses between the two phenomena and the law of the movement of the piston (Fig. 18).

The delays are thus avoided which might result either from the employment of a metallic manometer or from the propagation of the phenomena to an auxiliary vessel. Each number gives the average of from two to five experiments, made with electrolytic gas ($H_2 + O$) in a caoutchouc tube 5 mms. in diameter. We will first study the velocities, then the corresponding pressures, and lastly the limits of detonation.

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3. Velocities (per second).

Distance from the point of inflammation to the piston.	Durations observed.	Mean velocities from the beginning.	Mean velocities in each interval.
0·020 metres ...	0·000275 secs. ...	72·72 metres ...	72·7 metres
0·050 „ ...	0·000342 „ ...	146·20 „ ...	448·0 „
0·500 „ ...	0·000541 „ ...	924·40 „ ...	2261·0 „
5·250 „ ...	0·002108 „ ...	2491·00 „ ...	3031·0 „
20·190 „ ...	0·007620 „ ...	2649·00 „ ...	2710·0 „
40·430 „ ...	0·015100 „ ...	2679·00 „ ...	2706·0 „

Hence it is seen that the velocity increases rapidly from the starting point to the fifth cm., from which point the numbers obtained may be regarded as almost constant, at least within the limit of the errors of the experiments, which have a very considerable relative value at the commencement, for such short intervals.

The establishment of a regular system can only be effected successfully when the sparks that inflame the compound are strong enough. With feeble sparks, the period of variable condition can be greatly prolonged: over a space of 10 metres, mean velocities of 2126 metres and even 661 metres were thus obtained. Analogous phenomena are observed with the other explosive compounds. Electrolytic gas mixed with nitrogen, for example $H_2 + O + 2N$, gave a velocity of 41·9 metres per second in the two first cms., 1068 metres in the consecutive sections of 5·25 metres, and 1163 metres in the consecutive sections of 10 metres.

The influence of the initial inflammation is in this case still more marked, the velocity having fallen by accident to 445 and 435 metres, without any apparent change in the power of the initial spark; moreover, the nature of its product, in this case, indicated a different mode of combustion.

These discrepancies are not, in general, observed[1] with the process of registration based upon the employment of the fulminate interrupters, which tends to prove that the fulminate, by the sudden pressures

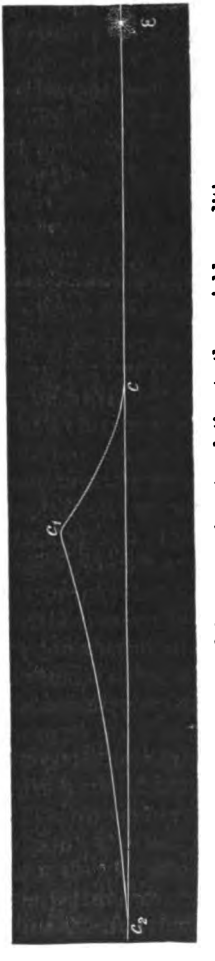

Fig. 18.—Traced from experiments relating to the variable condition.

[1] Mention may here be made of an experiment in which the compound $H_2 + O + N$ gave an exceptional velocity of 1564·5 metres, instead of the normal result 2121 metres; probably on account of the exceptional weakness of the priming.

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which it develops, helps the gaseous column to take up the detonation at once, which result it would attain later with less regularity by the ordinary inflammation.

4. *Pressures.*—These are deduced from the path traced by the piston.

For explosive gas ($H_2 + O$), the piston, placed at 2 cms. from the point of ignition, is projected forward at first by a pressure of 500 to 600 grms. per sq. cm., but this pressure falls very quickly, until it becomes *nil* and even negative (on account of the condensation of the aqueous vapour) at the end of ·0005 of a second.

At ·5 of a metre from the beginning, a pressure of 1·2 kgms. was found.

At 5·25 metres from the point of inflammation the first displacement of the piston took place under a pressure of about 5 kgms. per sq. cm.; and this pressure at the end of ·00125 of a second, was still more than 3 kgms.

Now, at this moment, the inflammation progressed 2·7 metres in a similar tube, according to the velocities mentioned above.

It will be seen, then, that in this part of the tube a considerable gaseous column, formed of aqueous vapour, is maintained at a high pressure, whereas at the beginning the pressure produced in one section by the combustion of the mixture is almost instantaneously annulled by the condensation of the sections in front of it; otherwise, the increase in pressures corresponds to the increase in velocity. It was found that the maximum of pressure developed by the mixture $H_2 + O$, burning in a closed vessel, is about 7 kgms. In this case the cooling influence of the sides of the vessel may be disregarded. In abnormal cases, when the rate of propagation falls below 2000 metres the pressure falls at the same time, which shows plainly the correlation of the two kinds of phenomena.

5. *Limits of Detonation.*—It is possibly due to similar causes that certain explosions of firedamp attain an exceptional rate of propagation and unusual violence. When the explosive wave is not propagated, combustion may still take place to a certain extent.

The limit of detonation in oxyhydrogen compounds is at about 22 per cent. of hydrogen, whereas the ordinary limit of combustion in mixtures of hydrogen and oxygen is at about 6 per cent. of hydrogen.

As the lower limit of detonation is approached the velocity of the wave falls considerably below the theoretical velocity (see above). The mixtures of cyanogen and nitric oxide such as $CN + 2NO$ show some points of interest. This compound, contained in an eudiometer, is exploded violently by a powerful spark. When ignited with a match it burns progressively. But, on the other hand, we did not succeed in propagating the

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explosive wave through the tubes. Here is found the same resistance to combustion that is characteristic of the compounds formed with nitric oxide (p. 63), a resistance that only disappears in compounds that are capable of developing an excessive temperature. In short, in the experiments described above, we did not observe any rate of propagation of the wave below 1000 metres per second.

Moreover, the propagation of the wave ceased whenever the theoretical temperature, T, of the compounds formed with free oxygen fell below 2000° (for hydrogen or cyanogen associated with nitrogen) or 1700° (for carbonic oxide or methane associated with nitrogen); figures corresponding to a lower limit of the energy of the molecules.

Finally, the propagation of the wave ceased every time the volume of the products of combustion amounted to less than the quarter (for hydrogen and nitrogen) or even the third (for methane or cyanogen associated with nitrogen) of the total volume of the final compound.

6. Taking all these observations into consideration, the propagation of the explosive wave is quite a distinct phenomenon from ordinary combustion. It only occurs when the layer ignited exercises the greatest possible pressure upon the next layer, *i.e.* when the ignited gaseous molecules possess the maximum velocity and consequently the maximum translating energy; which is simply the mechanical expression of the fact that they preserve almost the whole of the heat developed by the chemical reaction. This is shown by the approximate agreement of the calculations based upon the theoretical estimate of the translating energy with the values obtained by experiment for the velocity of the explosive wave. It is also shown by the correlative increase of the pressure and velocities towards the point of ignition.

7. The first coincidence shows, moreover, that dissociation has little influence in these phenomena; perhaps because it is restrained by the high pressure developed along the path of the wave and by its short duration. If this were not the case, the energy, and consequently the velocity, would fall far below the value calculated.

The influence of dissociation seems also annulled by the fact that the velocity of the wave is independent of the initial pressure (without admitting that dissociation is independent of the pressure).

8. It may, however, be remarked in conclusion, that it is the undulatory movement which is propagated, and not the gaseous mass which is transported with such great velocities. In fact, the velocity of the wave is the same, as has been shown, in a tube open at both ends, closed at one end and open at the other, or even closed at both ends.

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This result is also obtained in the experiments with the oxyhydrogen mixture, in which the same velocity was found either for the propagation of the flame (as attested by the destruction of the solid fulminate interrupters) or for the propagation of the pressure (as shown by the piston). The tracings also show that the pressure attains its maximum instantly upon the contact of the ignited layer with the layer immediately in front of it.

9. Several conditions contribute to the production of these effects. In the first place, it is necessary that the mass ignited at the commencement should not be too small, in order that radiation and conduction may not be given time to deprive this mass of an amount of heat, *i.e.* of energy, greater than that which is indispensable for the propagation of the wave. In fact, if the radius of the sphere ignited is equal to the thickness of the radiating layer, the loss of heat is proportionately greater than if the radiating layer is merely a fraction of this radius.

Moreover, when the number of molecules surrounding the point first ignited is too small they may not contain the combustive and the combustible elements in the exact ratio that corresponds to the average composition of the mixture; this would lower the temperature of this section, and consequently the energy of the molecules.

Another circumstance, no less important, is, that the elementary velocity of the chemical reactions, at the temperature of the combustion, should be sufficiently great for the heat given off in a given time to maintain the system at the point required; a condition which is all the more important when the elementary velocity of the reactions increases rapidly with the temperature. It can even be conceived that the explosive wave is only propagated if its theoretical velocity (rate of translation of the molecules) is below, or at the most equal to, the elementary velocity of the reaction.

10. Thus there is a limit in the condition that corresponds to the propagation of the explosive wave; this is the *régime of detonation.*

But it is easy to conceive quite a different limit, in which the excess of pressure of the ignited section upon the following one tends to fall to zero, and consequently the excess of velocity in the translation of the molecules, *i.e.* the excess of their energy, or, what is the same thing, the excess of heat which they contain, has the same tendency. In such a system the heat will be almost entirely lost by radiation, conduction, the contact of surrounding bodies and of inert gases, etc., with the exception of the very small quantity that is required for raising the adjacent portions to the temperature of combustion; this is *the régime of ordinary combustion,* to which the measure-

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ments of Bunsen, Schlœsing, and Mallard and Le Châtelier relate.

We may, moreover, imagine the existence of velocities that are intermediate between these two limits; but they do not constitute a regular system. In fact, the passing from one *régime* to the other is accompanied, as is generally the case with transitions of this kind, by violent movements, and extensive and irregular displacements of matter, during which the propagation of the combustion takes place in virtue of a vibratory movement increasing in amplitude and gaining in velocity.[1] Thus the *régime* of combustion, developed under conditions of continually increasing pressure, ends by arriving at the *régime* of detonation. These two *régimes*, and the general conditions that define the establishment of each of them, and the transition from one to the other, apply not only to gaseous explosive compounds, but also to solid and liquid explosive systems, seeing that the latter are wholly or partially transformed into gas, at the time of the detonation.

[1] See Mallard and Le Chatelier, "Comptes Rendus des séances de l'Académie des Sciences," tom. xcv. pp. 599, 1352.

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BOOK II.

THERMO-CHEMISTRY OF EXPLOSIVE COMPOUNDS.

CHAPTER I.

GENERAL PRINCIPLES OF THERMO-CHEMISTRY.

THERMO-CHEMISTRY is based on the following three fundamental principles:—

(1) MOLECULAR WORK. This furnishes the measure of chemical affinity.

(2) THE CALORIFIC EQUIVALENCE OF CHEMICAL TRANSFORMATIONS. The heat disengaged in a definite chemical transformation remains constant, like the sum of the weights of the elements.

(3) MAXIMUM WORK. The forecast of chemical phenomena is, in virtue of this principle, brought to the purely physical and mechanical notion of the maximum work accomplished by the molecular reactions.

FIRST PRINCIPLE—MOLECULAR WORK.

1. *The quantity of heat liberated in any reaction measures the sum of chemical and physical work accomplished in this reaction.*

Now the heat liberated in chemical action may be attributed to loss of energy, to changes of movement, and, lastly, to the relative changes which take place at the moment when the different molecules fly towards one another in order to form new compounds.

It follows from this principle that the heat liberated in a reaction is precisely equal to the amount of work which would have to be accomplished to restore the bodies to their primitive state. This work is at once chemical (changes of composition) and physical (changes of condition); the former alone can serve as measure of the affinities. We further see that the heat liberated in one and the same combination varies with the changes of state (solid, liquid, gaseous, or dissolved), with the external pressure, with the temperature, etc. Hence the necessity of defining all these conditions for each of the bodies experimented upon.

2. In general *the heat of molecular combination* which expresses

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the real work of the chemical forces (affinities) must be referred to the *reaction of perfect gases taking place at constant volume;* that is to say, that the components and the compounds must all be brought to the state of perfect gases and react in an unvarying space.

In the cases in which the reaction of the gases with formation of gaseous products gives rise to a change of volume at constant pressure the heat liberated necessarily varies with the temperature; but the variation is slight enough to be neglected, as long as we consider intervals of temperature which are not very far apart, and even up to 100° or 200°.

Table I. (p. 125) gives the principal data known on the subject. It expresses the heat liberated in reactions between gaseous bodies at constant pressure with formation of gaseous products.

3. In default of these conditions, which it is rarely possible to realise, it is permissible to refer the reactions of the bodies to the solid state; as has already been done in the case of the specific heats, according to the law of Dulong. In this state the influences of the external pressure and changes of temperature become only slightly sensible, and in consequence all bodies are more comparable than in the other states. The quantities of heat liberated hardly vary as long as the interval between the temperatures at which the reactions are carried out does not exceed 100° to 200°.

4. There remain the following definitions:—we shall term *exothermal* every reaction which liberates, and *endothermal* every reaction which absorbs heat.

Second Principle—The Calorific Equivalence of Chemical Transformations; otherwise termed Principle of the Initial and Final State.

If a system of simple or compound bodies, under given conditions, undergo physical or chemical changes capable of bringing it to a new state without giving rise to any mechanical effect exterior to the system, the quantity of heat liberated or absorbed by the effect of these changes depends solely on the initial and final state of the system. It is the same whatever the nature or the sequence of the intermediate states may be. This principle is demonstrated by the aid of the preceding, combined with the principle of energy. From it there follow various very important consequences, such as the following, which are simply stated, those who wish to go more fully into this subject being referred to the author's "Essai de Mécanique Chimique."

1°. *General Theorems on Reactions.*

Theorem I.—*The heat absorbed in the decomposition of a body is exactly equal to the heat at the time of the formation of the same compound, since the initial and final states are identical.*

This relation has been pointed out by Laplace and Lavoisier

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as far back as 1780. It enables us to measure the chemical work of electricity, of light, of heat, etc.

Theorem II.—*The quantity of heat liberated in a series of chemical and physical transformations accomplished successively or simultaneously, in one and the same operation, is the sum of the quantities of heat liberated in each isolated transformation,* (all the bodies being brought to absolutely identical physical conditions.)

It is in this way that the heat liberated by reactions referred to the solid state is calculated.

Theorem III.—*If two series of transformations be carried out, starting from two distinct initial states, and arriving at the same final state,* the difference between the quantities of heat liberated in the two cases will be precisely the quantity liberated or absorbed when the transformation is from one of the initial states to the other.

In this way is calculated the heat liberated by the union of water with acids, bases, anhydrous salts, by the synthesis of alcohols, etc.

The same theorem is employed to calculate the heat liberated by the transformation of an explosive substance, whenever this transformation does not occasion a total combustion, but the products are defined by analysis. In a word, it is sufficient to know, first, the heat produced by the total combustion of this substance, a heat which may be experimentally measured by detonating the substance in pure oxygen; second, the heat liberated by the total combustion of the products of explosion, which may be calculated when these products are known and well-defined. The difference between these two quantities represents the value sought.

Theorem IV.—The same conclusion is arrived at when *the two initial states are identical, the two final states being different.*

This relation serves as base to a number of calorimetric methods introduced into thermo-chemistry during the last few years, because it renders it unnecessary to define the intermediate states in complex reactions.

It is specially applicable to explosive substances when combustion is incomplete and gives rise to imperfectly known products. In short, it is sufficient to detonate the substance, first, in pure oxygen, which gives rise to total combustion; then in nitrogen, which yields incompletely burnt products. The heat liberated in each of the explosions is measured, and the difference between the two figures expresses the heat of combustion of the products of the second explosion; that is, the energy capable of being utilised in total combustion.

Theorem V.—*Substitutions.—If one body be substituted for another in a combination, the heat liberated by the substitution is the difference between the heat liberated by the direct formation of the new combination, and by that of the original combination.*

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This theorem is applicable to reciprocal replacements among the metals, the metalloids, bases, acids, etc.

Theorem VI.—*Indirect reactions.—If a compound yield one of its elements to another body, the heat liberated by this reaction is the difference between the heat liberated by the formation of the first compound, by means of the free element, and the heat liberated by the formation of the new compound, by means of the same free element.*

The theorem is applicable to indirect oxidations, hydrogenations, and chlorinations, to metallurgical reactions, to the study of explosive substances, etc.

In the latter study it gives the difference between the heat of combustion by free oxygen, and the heat of combustion by combined oxygen.

The oxidiser (nitrate, chlorate, bichromate, metallic oxide, etc.) is not a simple magazine of oxygen, as was formerly said; for generally this oxygen has lost a portion of its energy, equivalent to the heat of the first combination. In certain cases, on the contrary, such as where potassium chlorate is employed, the combined oxygen liberates more heat than the free would do.

Theorem VII.—*Slow reactions.—The heat liberated in a slow reaction is the difference between the quantities of heat liberated when the system of the components and that of the products of the slow reaction are brought by the aid of the same reagent to the same final state.*

This finds numerous applications in organic chemistry, in the study of ethers, amides, etc.

2°. *Theorems on the Formation of Salts.*

Theorem I.—*The heat of formation of a solid salt* is obtained by adding the heats liberated by the successive actions of the acid on water (Dt at the temperature t), of the base on water (D't), and of the dissolved acid on the dissolved base (Qt), then by subtracting from the sum the heat of solution of the salt (Δt), all being measured at the same temperature.

In general, calling S the heat liberated in the reaction of a system of solid bodies, transformed into a new system of solid bodies, by means of a solvent, we shall have—

$$S = \Sigma D t + Q t - \Sigma \Delta t.$$

Dt, D't, Qt, Δt, are obtained by experiment. They are quantities such that all of them vary considerably with the temperature t; while the quantity S is almost independent of the temperature —at least, within very wide limits, as will be presently shown.

Theorem II.—*The heat of formation of saline, acid, and alkaline hydrates is the difference between the heat of solution of the anhydrous body and that of the hydrated body, in the same proportion of water and at the same temperature.*

Theorem III.—*The heat of formation of a double crystallised salt is equal to the difference between the heat of solution of the*

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double salt and the sum of the heats of solution of the component salts, increased by the heat liberated by the mixture of the solutions of the separate salts, the whole at the same temperature and in presence of the same quantity of water.

Theorem IV.—*The heat of formation of acid salts is calculated* in a similar manner.

Theorem V.—*Changes of state of precipitates.—The difference between the quantities of heat liberated or absorbed during the re-dissolving of a precipitate, under two different states, at the same temperature, and in the same solvent is equal to the heat brought into action when the precipitate passes from one state to another.*

Theorem VI.—*Influence of dilution.—The heat of formation of dissolved salts varies in general with the dilution and temperature. The variation of this quantity of heat with the dilution at a given temperature* is expressed by the formula—

$$M' - M = \Delta - (\delta + \delta'),$$

M being the heat liberated by the reaction of an acid and a base, taken at a certain degree of concentration at this temperature; M′, the heat liberated by the same reaction, the two bodies being taken at a different degree of concentration; Δ the heat liberated (or absorbed) when the solution of the salt is brought from the degree of concentration corresponding to the first reaction to the concentration corresponding to the second. δ and δ′ are the analogous values, which correspond to the respective changes of concentration of the acid and of the base, always at the given temperature.

From a suitable degree of dilution, such as $100H_2O$ to 1 equiv. of an acid or of a base, the variation M′ − M generally reduces itself to negligable quantities, that is to say, within the limits of experimental error. But it should be remarked that the variation M′ − M ceases to be negligable, even within these limits, for salts formed by the union of bases with alcohols or *weak acids*, or by the union of any acid with *weak bases*, such as the metallic oxides. For such salts, moreover, the variation M′ − M tends to reduce itself to Δ, because δ and δ′ become inappreciable. Thus—

Theorem VII.—*Under these conditions the heat of dilution of the salt represents the variation in the heat of combination.*

This action of water constitutes a true characteristic of weak acids and bases. The preceding theorems are applicable not only to salts but to every compound, or system of compounds solid or in solution.

Theorem VIII.—*The reciprocal action of acids on the salts which they form with the same base,* in presence of the same quantity, of water, may be expressed at a given temperature by the relation

$$K_1 - K = M - M_1,$$

M, M_1 being the heats liberated by the separate union of the

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two acids with the base; K, K_1 the heats disengaged by the action of the salt formed by the other acid.

Theorem IX.—*Similarly the reciprocal action of bases on the salts which they form with the same acid*

$$K'_1 - K' = M - M_1.$$

Theorem X.—*The reciprocal action of the four salts formed by two acids and two bases* is expressed by the formula

$$K_1 - K = (M - M') - (M_1 - M'_1),$$

K being the heat liberated, when the solutions of two salts with different acids and bases (potassium sulphate and sodium nitrate) are mixed, and K_1 the heat liberated when the reciprocal pair are mixed (sodium sulphate and potassium nitrate). This theorem enables us to determine *the double saline decompositions* which are effected *in solutions*, when two salts of the same acid or the same base are unequally decomposed by the same quantity of water, which happens in the case of weak acids and bases, and the metallic oxides.

3°. *Theorems on the Formation of Organic Compounds.*

The heat of formation of organic compounds, by means of their elements, cannot be directly measured, but it may be calculated by the aid of various theorems, which follow from the second principle.

Theorem I.—*Difference between the heats of formation from the elements.—Let there be two distinct systems of compounds, formed from their elements, carbon, hydrogen, oxygen and nitrogen, or from very simple binary compounds, such as water, carbonic acid, carbonic oxide, ammonia; the difference between the heat of formation of the first system and that of the second is equal to the heat liberated when one of the systems is transformed into the other.*

It is in this way that the heat of formation of bodies belonging to the cyanogen series has been measured.

Theorem II.—*Difference between the heats of combustion.—The heat of formation of an organic compound by its elements is the difference between the sum of the heats of total combustion of its elements by free oxygen and the heat of combustion of the compound with formation of identical products.*

It is in virtue of this principle that most of the heats liberated by the formation of organic compounds and their reciprocal transformations have been obtained.

Theorem III.—*Conversely, the heat of combustion of a body formed of carbon, hydrogen, oxygen and nitrogen, is calculated by means of its heat of formation. It is sufficient to find the sum of the quantities of heat liberated when the carbon and hydrogen supposed free, which enter into the composition of this body, are changed into water and carbonic acid, and to deduct from this sum the* heat of formation.

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Theorem IV.—*Formation of alcohols.—The heat liberated when an alcohol is formed by the union of water and of a hydrocarbon is the difference between the quantities of heat liberated when the alcohol and the hydrocarbon form one and the same combination with an acid such as sulphuric acid.*

The formation and the decomposition of conjugate bodies (ethers, amides, etc.) give rise to various other theorems, analogous to those relative to the salts, but which are omitted in order not to unduly extend this summary.

4°. *Theorems relative to the Variation of the Heat of Combination with the Temperature.*

In general, the quantity of heat liberated in a chemical reaction is not a constant quantity; it varies with the changes of state, as has been said above; but it also varies with the temperature, even when each one of the reacting substances preserves the same physical state during the interval considered. This variation is calculated in the following manner for any reaction whatever, according to the second principle.

The reaction may be determined at an initial temperature, t, and the heat liberated, Qt, may be measured.

The component bodies may also be raised separately from the temperature t to the temperature T: which absorbs a quantity of heat, U, depending on the changes of state and of the specific heats, then the reaction is determined, which liberates Qt; lastly, the products are brought by a simple lowering of temperature from T to t, which liberates a quantity of heat, V, also depending on the changes of state and of the specific heats. The initial and final states being the same in both processes the quantities of heat liberated are equal, that is to say:—

Theorem I.—*The difference between the quantities of heat liberated by the same reaction, at two distinct temperatures, is equal to the difference between the quantities of heat absorbed by the components and by their products, during the interval of the two temperatures.*

$$QT = Qt + U - V.$$

U − V represents the variation in the heat of combustion.

Theorem II.—If, *during the interval* T − t, *none of the original or final bodies undergoes change of state, this expression reduces itself to the sum of the mean specific heats of the first bodies during this interval, minus the sum of the mean specific heats of the second bodies, multiplied by the interval of the temperatures.*

$$U - V = (\Sigma c - \Sigma c_1)(T - t).$$

The heat of combination will go on increasing or diminishing with the temperature, and may even change in sign, according as the first sum is greater than the second, or *vice versâ*.

Theorem III.—*Gaseous combinations formed without condensation.*—In order that *the heat liberated may be independent of the temperature,* the two above sums must be equal. Now this

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equality exists in fact for compound gases formed without condensation. It is admitted that it should exist in principle for perfect gases, if the combination were effected at constant volume, hence the definition (p. 114) of the molecular heat of combination.

Theorem IV.—*Combinations referred to the solid state.*—The same equality exists approximately for solid bodies; the specific heat of these compounds, referred to equivalent weights, being nearly the same as the sum of those of their components. The heats of combination can therefore be referred to the solid state, as validly as the atomic specific heats already are by Dulong's law; which shows the importance of the expression S given above. The liquid or dissolved state does not present the same advantages; for instance, the heat liberated in the reaction of dilute hydrochloric acid on dilute soda, these two bodies being taken at a given degree of concentration, varies from + 14·7 Cal. to + 10·4 Cal., between 0 and 100°, that is to say, nearly by half the latter's value.

Theorem V.—*The heat liberated or absorbed during solution of an anhydrous salt changes continually in amount with the temperature of solution;* since the specific heat of saline solutions differs, generally speaking, from the sum of the specific heats of the salt and water taken separately.

It is smaller with the majority of the dilute solutions formed by the inorganic salts. But the contrary holds good with the solutions of various organic salts. *The heat of solution of anhydrous salts changes as a rule even in sign,* for an interval in temperature not exceeding 100° to 200°; sometimes this change of sign occurs near the surrounding temperature, and can be determined by direct experiments.

Hence it follows that those of the inorganic salts which produce cold when dissolving in water, at the ordinary temperature, produce on the contrary heat at a higher temperature, whence it also follows that *there exists a temperature for which no thermal variation is produced during solution.*

These results, of which the development and demonstration will be found in the author's "Essai de Mécanique Chimique," tom. i. p. 123, et seq., prove that solution has hitherto erroneously been assimilated to fusion.

5°. *Theorems relative to the Variation of the Heat of Combination with the Pressure.*

Theorem I.—*In gaseous combinations and reactions the heat liberated is independent of the pressure, operating at a constant volume.*

This statement is no other than Joule's law, and is only true for slight pressures and on the assumption that there is no appreciable internal work in the gases, this work being in fact negligible for gases remote from the point of liquefaction and at a low pressure.

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Theorem II.—*In gaseous combinations and reactions effected without condensation, the heat liberated is the same, whether at constant volume or at constant pressure.*

Such is the case with the combustion of cyanogen, whether by free oxygen or nitric oxide.

Theorem III.—*In reactions effected with condensation* the heat liberated at a constant pressure, p, at the atmospheric pressure for example, and at a given temperature, t, is connected with the heat liberated at constant volume, v, and at the same temperature, by the following relation—

$$Qtv = Qtp + 0{\cdot}542\ (N' - N) + 0{\cdot}002t.$$

N here expresses the quotient by 22·32 of the number of litres occupied by the component gases reduced to 0° and 0·760 metres, and N′ the same quotient for the resulting gases.

This theorem is of great importance in calorimetric measurements relative to explosive substances. It enables the difference between the two quantities of heat at constant pressure and volume to be calculated for every reaction of which the formula is known (see p. 15). It is not only applicable to reactions where all the bodies, components as well as products, are gaseous, but also to those where some of them only possess the solid or liquid state at the outset, or assume it at the end.

Third Principle—Maximum Work.

Every chemical change, effected without the intervention of a foreign energy, tends towards the production of the body or of the system of bodies liberating the most heat.

The necessity of this principle may be seen by observing that the system which has liberated the greatest possible amount of heat, no longer possesses in itself the energy necessary for effecting a new transformation. Every fresh change requires work, which cannot be performed without the intervention of a foreign energy. On the other hand, a system still capable of liberating heat by a fresh change possesses the energy necessary for effecting this change without any auxiliary intervention.

The *foreign energies* here in question are those of physical agents: light, electricity, heat; the energy of disaggregation developed by solution; lastly, the energy of chemical reactions, simultaneous to that under consideration. Now, the intervention of electric or luminous energies in a chemical phenomenon is ordinarily apparent, and it is the same with chemical energy, borrowed from a simultaneous reaction. The only cases which call for discussion are those in which calorific energy and the energy of disaggregation by solution intervene. They are distinguished by the following general character, that these energies are exercised solely to regulate *the conditions of existence of each compound regarded separately* without in any other way intervening in the place of the reciprocal chemical actions.

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Thus they are manifested under the conditions where they provoke either the change of physical state (liquefaction, vaporisation) of any one of the bodies experimented on, regarded separately, or its isomeric modification, or its total or partial decomposition. It is furthermore evident, generally speaking, that a compound can only take part in a reaction, if it exist in *the isolated state* under the conditions of the experiment, and in the proportion in which it can exist. This remark rightly understood, can, strictly speaking, be made to apply in practice, for it is sufficient to regard each of the components and of the products in a system, and to know its individual state of stability or of dissociation, under given conditions, in order to be able to apply the principle. It is, moreover, necessary to take into account in calculations and reasonings all the compounds capable of existing under the conditions of the experiment, such as double salts, acid salts, perchlorides, hydrates, etc., and secondary compounds of every kind, which are ordinarily neglected in the general interpretation of reactions, but each of which contributes its quota, and, so to speak, its weight to the thermal balance of affinities.

Lastly, let us note that in the calculation of the quantities of heat liberated by a transformation, *we should consider*, as far as possible, *the corresponding bodies in the initial and final system* taking them *under the same physical state*. This mode of proceeding offers the advantage of putting aside, without further discussion, a whole class of foreign energies, such as the energies consumed in changes of physical state.

We do not wish to enter here upon more extended developments; it will suffice to refer the reader to the detailed discussion which is to be found in "Essai de Mécanique Chimique."[1] There it will be seen how the third principle is deduced from the experimental study of the phenomena of combination and decomposition.[2]

The following theorems are given which are applicable to a large number of phenomena:—

Theorem I.—*No endothermal reaction is possible without the intervention of foreign energies.*

Theorem II.—*A system is the more stable, everything else being equal, the larger the fraction of its energy which it has lost.*

Theorem III.—*Every chemical equilibrium results from the intervention of certain dissociated compounds, that is to say, in the state of partial and reversible decomposition, which act at once by themselves, as compounds, and by their components.*

Under these conditions, there always intervene, in opposition to the chemical energies properly so called, foreign energies, electric or calorific, the latter especially.[3]

[1] Tom. ii. pp. 421–471. [2] Ibid. pp. 424–438.
[3] "Essai de Mécanique," chap. ii. pp. 439 and following.

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Exothermal reactions are, as has just been said, the only ones which can be effected without the aid of a foreign energy. However, they often require, in order to start them, the intervention of a certain preliminary work, analogous to ignition.

Theorem IV.—*An exothermal reaction which does not take place of itself at a certain temperature, can almost always take place of itself at a higher temperature, that is to say, in virtue of the work of heating.*

Theorem V.—*It can likewise take place at the ordinary temperature, with the aid of a suitable auxiliary work, and especially with the aid of chemical work, due to a simultaneous and correlative reaction.*

Theorem VI.—*Within the limits of temperature at which exothermal reactions take place, they do so, generally speaking, more rapidly the higher the temperature.*

Theorem VII.—*Successive transformations can only take place directly without the intervention of foreign energies, if each of the transformations, regarded separately, as well as their definite sum, be accompanied by a liberation of heat.*

In other words, the energy proper to a system may be expended either all at once, or little by little, and according to several distinct cycles, but there cannot be a gain of energy, due to the internal actions alone, in any of the intermediate changes. We shall give lastly, a theorem of the greatest importance in the study of saline and many other reactions.

Theorem VIII.—*Every chemical reaction capable of being accomplished without the aid of preliminary work and independent of the intervention of an energy foreign to that of the bodies present in the system, is of necessity produced, if it liberate heat.*

It is in virtue of the third principle that the forecast of chemical phenomena is reduced to the purely physical and mechanical notion of maximum work effected by the molecular actions.

5. *Numerical Tables.*

The following tables give the principal data relative to the quantities of heat liberated by the formation of compounds used, or capable of being used, as explosives.

In these tables the authorities for the different determinations are indicated by their initials, viz.:—

Al = Alluard	Gh = Graham	Pf = Pfaundler
An = André	G = Grassi	Rech = Rechenberg
A = Andrews	Ha = Hammerl	R = Regnault
B = Berthelot	H = Hautefeuille	Sab = Sabatier
Cal = Calderon	Hs = Hess	Sa = Sarrau
Ch = Chroutschoff	Jo = Joannis	S = Silbermann
Ds = Desains	L = Louguinine	T = Thomsen
Dv = Deville	M = Mitscherlich	Tr = Troost
Dt = Ditte	Og = Ogier	Vie = Vieille
D = Dulong	P = Person	Vi = Vielle
F = Favre	Pett = Pettersen	W = Woods

*** The authority preferred is bracketed; F. & S. [T].

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TABLE I.—FORMATION OF GASES BY THE UNION OF THE GASEOUS ELEMENTS, THE COMPOUNDS BEING REFERRED TO THE SAME VOLUME, 22 LITRES (1 + αt), UNDER NORMAL PRESSURE.

Names.	Elements.	Equivalent of gaseous components.	Heat.	Authorities.
Hydrochloric acid	$H + Cl$	36·5	+ 22·0	T. B.
Hydrobromic acid	$H + Br$	81	+ 13·5	T. [B.]
Hydriodic acid	$H + I$	128	− 0·8	T. B.
Water	$H_2 + O$	9 × 2	+ 29·5 × 2	(1)
Hydrogen sulphide	$H_2 + S$	17 × 2	+ 3·6 × 2	T. H.
Ammonia	$H_3 + N$	17	+ 12·2	B. T.
Nitrogen monoxide	$N_2 + O$	22 × 2	− 10·3 × 2	F. & S. [B.]
Nitric oxide	$N + O$	30	− 21·6	[B.] T.
Nitrogen trioxide	$N_2 + O_3$	38 × 2	− 11·1 × 2	B.
Nitric peroxide	$N + O_2$	46	− 2·6	B.
Nitrogen pentoxide	$N_2 + O_5$	54 × 2	− 0·6 × 2	B.
Nitric acid	$N + O_2 + H$	63	+ 34·4	B.
Chlorine monoxide	$Cl_2 + O$	43·5 × 2	− 7·6 × 2	T. B.
Sulphur chloride	$S_2 + Cl_2$	67·5 × 2	+ 8·1 × 2	Og.
„ dioxide	$S + O_2$	32 × 2	+ 35·8 × 2	[B.] F. & S.
„ trioxide	$S + O_3$	40 × 2	+ 48·2 × 2	B.
„ trioxide	$SO_3 + O$	40 × 2	+ 12·4 × 2	B.
„ oxychloride	$SO_2 + Cl_2$	67·2 × 2	+ 6·6 × 2	Og.
Ozone	$O + O_2$	24 × 2	− 14·8 × 2	B.
Carbon dioxide	$CO + O$	22 × 2	+ 34·1 × 2	(2)
„ oxychloride	$CO + Cl_2$	49·5 × 2	+ 9·4 × 2	B.
„ oxysulphide	$CO + S$	30 × 2	− 1·8 × 2	B.
Hydrocyanic acid	$CN + H$	27	+ 7·8	B.
Cyanogen chloride	$CN + Cl$	61·5	+ 1·6	B.
Ethane	$C_2H_4 + H_2$	30	+ 21·1	B.
Propane	$C_3H_6 + H_2$	44	+ 22·8	B.
Dibromethane	$C_2H_4 + Br_2$	188	+ 29·1	B.
Glycolic ether	$C_2H_2 + O$	44	+ 33·0	B.
Aldehyde	$C_2H_2 + O$	44	+ 65·9	B.
Acetic acid	$C_2H_4 + O_2$	60	+ 13·3	B.
Alcohol	$C_2H_4 + H_2O$	46	+ 16·9	B.
Formic acid	$CO + H_2O$	46	+ 3·1	B.
„ „	$CO_2 + H_2$	46	− 5·8	B.
Chlorethane	$C_2H_4 + HCl$	64·5	+ 31·9	B.
Bromethane	$C_2H_4 + HBr$	109	+ 32·9	B.
Iodethane	$C_2H_4 + HI$	156	+ 39·0	B.
Ethyl acetate	$C_2H_4 + C_2H_4O_2$	88	+ 13·2	B.
Ethylidene chloride	$C_2H_2 + 2HCl$	97	+ 29 × 2	B. & Og.
Amyl chloride	$C_5H_{10} + HCl$	106·5	+ 16·9	B.
„ bromide	$C_5H_{10} + HBr$	151	+ 13·2	B.
„ iodide	$C_5H_{10} + HI$	198	+ 10·6	B.
Nitric acid	$N_2O_4 + H_2O$	63	+ 5·3	B.
Acetic acid	$C_4H_6O_3 + H_2O$	60	+ 10·0	B.
Chloral hydrate	$C_2HCl_3O + H_2O$	...	+ 2·0	B.
„ alcoholate	$C_2HCl_3O + C_2H_6O$	...	+ 1·6	B.
Diamylene	$2C_5H_{10}$	140	+ 15·4	B.
Benzene	$3C_2H_2$	78	+ 171	B.
„	C_6H_6	78	+ 70·5	B.
Aldehyde	C_2H_4O	44	+ 32·9	B.

[1] D. Hs. F. & S. G. A. T. B.

[2] D. F. & S. G. A. B. T.

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TABLE II.—FORMATION OF SOLID SALTS FROM THE ANHYDROUS ACID AND BASE, BOTH SOLID.

NITRATES.

$N_2O_5 + H_2O$	(solid)	+ 1·1
$N_2O_5 + K_2O$	„	+ 64·2
$N_2O_5 + Na_2O$	„	+ 54·4
$N_2O_5 + BaO$	„	+ 40·7
$N_2O_5 + SrO$	„	+ 38·1
$N_2O_5 + CaO$	„	+ 29·6
$N_2O_5 + PbO$	„	+ 21·4
$N_2O_5 + Ag_2O$	„	+ 19·2

IODATES.

$I_2O_5 + K_2O$	(solid)	+ 51·6
$I_2O_5 + BaO$	„	+ 34·9

SULPHATES.

$SO_3 + H_2O$	(solid)	+ 9·9
$SO_3 + K_2O$	„	+ 71·3
$SO_3 + Na_2O$	„	+ 61·7
$SO_3 + BaO$	„	+ 51·0
$SO_3 + SrO$	„	+ 47·8
$SO_3 + CaO$	„	+ 42·0
$SO_3 + PbO$	„	+ 30·4
$SO_3 + ZnO$	(solid)	+ 19·7
$SO_3 + CuO$	„	+ 19·5
$SO_3 + Ag_2$	„	+ 28·0

OTHER SALTS.

PHOSPHATES.

$P_2O_5 + 3H_2O$	(solid)	+ 4·9
$P_2O_5 + 3Na_2O$	„	+ 39·8
$P_2O_5 + 3CaO$	„	+ 26·7

SUCCINATES.

$C_4H_4O_3 + H_2O$	(solid)	+ 4·1
$C_4H_4O_3 + Na_2O$	„	+ 38·1

CARBONATES.

CO_2	(solid)	+ K_2O	+ 40·3
CO_2	„	+ Na_2O	+ 34·9
CO_2	„	+ BaO	+ 25·0
CO_2	„	+ CaO	+ 18·7

TABLE III.—FORMATION OF SOLID SALTS FROM THE GASEOUS ANHYDROUS ACID AND THE SOLID BASE.

Names.	Elements.	Heat disengaged.
Nitrates	$N_2O_5 + K_2O$	+ 70·7
	$N_2O_5 + Na_2O$	+ 60·9
	$N_2O_5 + BaO$	+ 47·8
Nitrites	$N_2O_3 + BaO$	+ 33·8
Sulphates	$SO_3 + K_2O$	+ 76·6
	$2SO_3 + K_2O$	+ 95·7
	$SO_3 + Na_2O$	+ 67·2
	$SO_3 + BaO$	+ 56·9
Sulphites	$SO_2 + K_2O$	+ 53·1
	$2SO_2 + K_2O$	+ 66·8
Acetates	$C_4H_6O_3 + K_2O$	+ 55·1
	$C_4H_6O_3 + Na_2O$	+ 47·0
	$C_4H_6O_3 + BaO$	+ 35·5
Carbonates	$CO_2 + K_2O$	+ 43·3
	$CO_2 + Na_2O$	+ 37·9
	$CO_2 + BaO$	+ 28·0
	$CO_2 + SrO$	+ 26·7
	$CO_2 + CaO$	+ 21·7
	$CO_2 + PbO$	+ 10·8
	$CO_2 + Ag_2O$	+ 9·8

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TABLE IV.—FORMATION OF SOLID SALTS FROM HYDRATED ACID AND BASE, BOTH SOLID.

Acid + base = salt + water (solid).

The heat disengaged, S, has the property of not varying sensibly with the temperature contrariwise to what happens in the reactions of dissolved bodies (p. 117). ("Annales de Chimie et de Physique," 5e série, tom. iv. p. 74.)

Symbol of the metals.	Nitrates. NO_3M.	Formates.	Acetates.	Benzoates.	Picrates.	Sulphates.	Oxalates.	Tartrates.
K .	+ 42·6	+ 25·5	+ 21.9	+ 22·5	+ 30·5	+ 40·7	+ 29·4	+ 27·1
Na .	+ 36·1	+ 22·3	+ 18·3	+ 17·4	+ 24·3	+ 34·7	+ 26·5	+ 22·9
Ba .	+ 31·7	+ 18·5	+ 15·2	...	...	+ 33·0	+ 20·8[1]	...
Sr .	+ 29·2	+ 16·7	+ 14·7	...	...	+ 29·5	+ 21·3	...
Ca .	...	+ 13·5	+ 10·6	+ 8·2	...	+ 24·7	+ 18·9	+ 16·7[1]
Mn .	...	+ 7·6	+ 4·5	...	...	+ 15·6	+ 13·2	...
Zn .	...	+ 6·2	+ 3·3	Phenate.	Succinates.	+ 11·9	+ 11·5	Iodates.
Cu .	...	+ 5·4	+ 4·3	K + 17·7	K + 23·2	+ 10·5	...	K + 31·5
Pb .	+ 19·7	+ 9·1	+ 5·1		Na + 20·0	+ 19·9	+ 13·1	Ba + 25·6
Ag .	+ 18·0	...	+ 7·6			+ 17·9	+ 12·5	...

[1] This number refers to precipitated salts which contain combined water.

TABLE V.—FORMATION OF SOLID AMMONIACAL SALTS.

Names.	Components.	Heat disengaged.
(1) From the solid hydrated acid and gaseous base.		
Nitrate	$HNO_3 + NH_3$	+ 34·0
Formate	$CH_2O_2 + NH_3$	+ 21·0
Acetate	$C_2H_4O_2 + NH_3$	+ 18·5
Benzoate	$C_7H_6O_2 + NH_3$	+ 17·0
Picrate	$C_6H_3(NO_2)_3O_7 + NH_3$	+ 22·9
Sulphate	$H_2SO_4 + 2NH$	+ 33·8
Oxalate	$C_2H_2O_4 + 2NH_3$	+ 24·4
Succinate	$C_4H_6O_4 + 2NH_3$	+ 19·7
(2) Acid and base gaseous.		
Chloride	$HCl + NH_3$	+ 42·5
Bromide	$HBr + NH_3$	+ 45·6
Iodide	$HI + NH_3$	+ 44·2
Cyanide	$HCy + NH_3$	+ 20·5
Sulphide	$H_2S + NH_3$	+ 23·0
Acetate	$C_2H_4O_2 + NH_3$	+ 26·0
Formate	$CH_2O_2 + NH_3$	+ 29·0
Nitrate	$HNO_3 + NH_3$	+ 41·9
Trimethylamine chloride	$HCl + C_3H_9N$	+ 39·8
(3) From the anhydrous oxyacid, water, and the base, all three gaseous.		
Nitrate	$N_2O_5 + H_2O + 2NH_3$	+ 47·1
Nitrite	$N_2O_3 + H_2O + 2NH_3$	+ 33·7
Acetate	$C_2H_2O + H_2O + NH_3$	+ 41·5
Sulphate	$SO_3 + H_2O + 2NH_3$	+ 53·5
Bicarbonate	$CO_2 + H_2O + NH_3$	+ 30·4
Formate	$CO + H_2O + NH_3$	+ 31·6
(4) From their gaseous elements.		
Chloride	$Cl + H_4 + N$	+ 76·7
Bromide	$Br\ (gas) + H_4 + N$	+ 71·2
Iodide	$I\ (gas) + H_4 + N$	+ 56·0
Sulphide	$S\ (gas) + H_4 + N$	+ 42·4
Nitrite	$O_2 + H_4 + N_2$	+ 64·8
Nitrate	$O_3 + H_4 + N_2$	+ 87·9
Perchlorate	$Cl + O_4 + H_4 + N$	+ 79·7
Sulphate	$S + O_4 + H_4 + N_2$	+ 142·4
Hydroxylamine Chloride	$Cl + H_4 + N + O$	+ 70·8

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TABLE VI.—FORMATION OF THE PRINCIPAL CHEMICAL COMBINATIONS, THE COMPONENTS AND THE COMPOUNDS BEING TAKEN IN THEIR ACTUAL STATE AT + 15°. METALLOIDS.

Names.	Components.	Compounds.	Equivalent of compound.	Heat disengaged, the compounds				Authorities.
				Gaseous.	Liquid.	Solid.	Dissolved.	
COMPOUNDS CONTAINING HYDROGEN.								
Hydrochloric acid	$H + Cl$	HCl	36·5	+ 22·0	...	...	+ 39·9	T. B.
Hydrogen perchloride	HCl conc. $\times Cl_2$	HCl_3	107·5	...	...	...	+ 9·4	B.
Hydrobromic acid	$H + Br$	HBr	81	+ 9·5	...	...	+ 29·5	T. (B.)
Hydriodic acid	$H + I$	HI	128	− 6·2	...	...	+ 13·2	T. B.
Water	$H_2 + O$	H_2O	9	+ 29·1	+ 34·5	+ 35·2	...	D. Hs. F. & S. G. A. T. B.
Hydrogen peroxide	$H_2 + O_2$	H_2O_2	17	...	...	...	+ 23·7	F. & S. T. (B.)
	$H_2O + O$	H_2O_2	17	...	...	...	− 10·8	F. & S. G. T. (B.)
Hydrogen sulphide	$H_2 + S$	H_2S	17	+ 2·3	...	...	+ 4·6	H. T.
Hydrogen persulphide	$H_2S + Sn$	$H_2Sn + 1$	...	...	− 2·6	...	...	Sab.
Hydrogen selenide	$H_2 + Se$	H_2Se	40·5	− 2·7	...	...	...	H.
Ammonia	$H_3 + N$	NH_3	17	+ 12·2	...	...	+ 21·0	(B.) T.
Hydroxylamine	$N + H_3 + O$	NH_3O	33	...	...	...	+ 19·0	B.
Hydrogen phosphide (gaseous)	$H_3 + P$	PH_3	34	+ 11·6	...	...	...	Og.
Hydrogen phosphide (solid)	$H + P_2$	P_2H	63	...	...	+ 17·7	...	Og.
Hydrogen arsenide (gaseous)	$H_3 + As$	AsH_3	78	− 36·7	...	...	...	Og.
Phosphonium bromide	$PH_3 + HBr$	PH_4Br	115	...	...	+ 23·0	...	Og.
Phosphonium iodide	$PH_3 + HI$	PH_4I	162	...	...	+ 24·0	...	Og.
Acetylene or ethine (C diamond)	$C_2 + H_2$	C_2H_2	13	− 30·5	...	...	...	(B.) T.
Ethylene (C diamond)	$C_2 + H_4$	C_2H_4	14	− 7·7	...	...	...	D. F. & S. A. (B.) T.
Ethane (C diamond)	$C_2 + H_6$	C_2H_6	15	+ 2·85	...	...	...	B.
Methane (C diamond)	$C + H_4$	CH_4	16	+ 18·5	...	...	...	D. F. & S. A. (B.) T.
Silicium hydride	$Si + H_4$	SiH_4	32	+ 32·9	...	...	...	Og.
COMPOUNDS CONTAINING OXYGEN AND SULPHUR.								
Nitrogen monoxide	$N_2 + O$	N_2O	22	− 10·3	− 8·1	...	...	F. & S. T. (B.)
Nitric oxide	$N + O$	NO	30	− 21·6	...	...	...	B. T.
Nitrogen trioxide	$N_2 + O_3$	N_2O_3	38	− 11·6	...	...	- 4·2	B.
Nitric peroxide	$N + O_2$	NO_2	46	− 2·6	+ 1·7	...	...	B.
Nitrogen pentoxide	$N_2 + O_5$	N_2O_5	54	− 0·6	+ 1·8	+ 5·9	+ 14·3	B.
Nitric acid	$N_2 + O_5 + H_2O$	HNO_3	63	− 0·1	+ 7·1	+ 7·7	+ 14·3	B.
	$N_2 + O_6 + H_2$	HNO_3	63	+ 34·4	+ 41·6	+ 42·2	+ 48·8	B.

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Nitric acid (hydrate)	$HN+O_3+2H_2O$	$HNO_3,2H_2O$	99	...	+ 5·0	...	...	B.
Nitrogen sulphide	N_2+S_2	N_2S_2	46	...	...	− 32·3	+ 42·9	B. & Vie.
Sulphurous anhydride	$S+O_2$	SO_2	32	+ 34·6	...	...	+ 38·8	F. & S. T. (B.)
Sulphuric anhydride	$S+O_3$	SO_3	40	+ 45·9	...	+ 51·8	+ 70·5	D. H. F. & S. A. T. (B.)
Sulphuric acid (monahydrate)	SO_2+O+H_2O	SO_3H_2O	49	...	+ 27·2	...	+ 36·0	D. H. F. & S. A. T. (B.)
	$S+O_4+H_2O$	SO_3H_2O	49	...	+ 62·0	+ 62·4	+ 70·5	D. H. F. & S. A. T. (B.)
	$S+O_4+H_2$	SO_4H_2	49	...	+ 96·5	+ 96·9	+ 105·0	D. H. F. & S. A. T. (B.)
Sulphuric acid (dihydrate)	$SO_4H_2+H_2O$	$SO_4H_2H_2O$	58	...	+ 3·1	+ 4·5	...	B.
	S_2+O_7	S_2O_7	88	...	...	...	+ 126·6	B.
Persulphuric acid, or	S_2O_6diss. $+O$	S_2O_7	88	...	...	...	− 13·8	B.
Hypophosphorous acid	P_2+O+3H_2O	H_3PO_2	66	...	+ 55·0	+ 37·4	+ 37·2	T.
Phosphorous acid	$P_2+O_3+3H_2O$	H_3PO_3	82	...	+ 122·1	+ 125·1	+ 125·0	T.
Phosphoric anhydride	P_2+O_5	P_2O_5	71	...	...	+ 181·9	+ 202·7	T.
Phosphoric acid	$P_2+O_5+3H_2O$	H_3PO_4	98	...	+ 197·5	+ 200·0	+ 202·7	T.
Arsenious acid	As_2+O_3	As_2O_3	99	...	...	+ 77·3	+ 73·5	T.
Arsenic acid	As_2+O_5	As_2O_5	115	...	...	+ 109·7	+ 112·7	T.
Boric acid (Bamorphous)	B_2+O_3	B_2O_3	35	...	...	+ 156·3	+ 159·9	B. Tr. & H.
Hypochlorous oxide	Cl_2+O	Cl_2O	43·5	− 7·6	...	...	− 2·9	B. T.
Chloric acid	$Cl_2+O_5+H_2O$	$HClO_3$	84·5	...	...	...	− 12·0	(B.) T.
Perchloric acid	$Cl_2+O_7+H_2O$	$HClO_4$	100·5	...	− 15·4	...	+ 4·9	B.
„ „ (2nd hydrate)	$HClO_4+H_2O$	$HClO_4H_2O$	118·5	...	+ 12·6	+ 8·6	...	B.
„ „ (3rd hydrate	$HClO_4+2H_2O$	$HClO_42H_2O$	136·5	...	...	+ 15·0	...	B.
Hypobromous oxide	Br_2+O	Br_2O	88	...	...	...	− 6·2	B.
Bromic acid	$Br_2+O_5+H_2O$	$HBrO_3$	129	...	...	...	− 24·8	T. B.
Hypoidous oxide	I_2+O	I_2O	135	...	...	...	− 5·2	B.
Iodic oxide	I_2+O_5	I_2O_5	167	...	...	+ 22·8	+ 21·9	T. B.
Iodic acid	$I_2+O_5+H_2O$	HIO_3	176	...	...	+ 24·3	+ 21·9	T. B.
Periodic acid	$I_2+C_7+H_2O$	HIO_4	192	...	...	...	+ 13·5	T.
Carbon dioxide (C diamond)	$C+O_2$	CO_2	22	+ 47·0	...	+ 50·0	+ 49·8	
Carbon dioxide (C amorphous)				+ 48·5	...	+ 51·5	+ 51·3	F. & S.
Carbon monoxide (C diamond)	$C+O$	CO	14	+ 12·9	...	...	...	
Carbon monoxide (C amorphous)				+ 14·4	...	...	...	F. & S. Cy. A. T. (B.)
Carbon oxychloride (C diamond)	$C+O+Cl_2$	$COCl_2$	49·5	+ 22·3	...	...	...	
Carbon oxychloride (C amorphous)				+ 23·8	...	...	...	B.
Carbon oxychloride	$CO+Cl_2$	$COCl_2$	49·5	+ 9·4	...	...	...	B.
Carbon oxysulphide (C diamond)	$C+O+S$	COS	30	+ 9·8	...	...	...	
Carbon oxysulphide (C amorphous)				+ 11·3	...	...	...	B.
Oxysulphide	$CO+S$	COS	30	− 3·1	...	...	...	B.
Carbon disulphide (C diamond)	$C+S_2$	CS_2	38	− 10·55	− 7·2	...	...	
Carbon disulphide (C amorphous)				− 9·05	− 5·7			F. & S. (B.)
Silica (Si amorphous)	$Si+O_2$	SiO_2	60	...	...	+ 219·2	+ 207·4	Tr. & H. B.
Silica (Si crystallized)						+ 211·1	+ 199·3	Tr.

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TABLE VII.—FORMATION OF METALLIC OXIDES ACCORDING TO M. THOMSEN.[1]

Name.	Components.	Equivalents.	Heat disengaged.	
			Solid state.	Dissolved state.
Potash	$K_2 + O$ (Beketoff)	47·1	+ 48·6	+ 82·3
	$K_2 + O + H_2O$	56·1	+ 69·8	+ 82·3
	$K_2 + H_2 + O_2$	...	+ 104·3	+ 116·8
Soda	$Na_2 + O$ (Beketoff)	31	+ 50·1	+ 77·6
	$Na_2 + O + H_2O$	40	+ 67·8	+ 77·6
	$Na_2 + H_2 + O_2$	...	+ 102·3	+ 112·1
Ammonia	$N + H_3 + H_2O$	...	...	+ 21·0
	$N + H_3 + O$	35	...	+ 90·0
Lime	$Ca + O$	28	+ 66·0	+ 75·05
	$Ca + O + H_2O$	37	+ 73·5	+ 75·05
	$Ca + H_2 + O_2$	37	+ 108·0	+ 109·55
Strontia	$Sr + O$	51·8	+ 65·7	+ 79·1
	$Sr + O + H_2O$	60·8	+ 74·3	+ 79·1
	$Sr + H_2 + O_2$	60·8	+ 108·8	+ 113·6
Baryta	$Ba + O$	76·5	x	x + 14·0
Barium dioxide	$BaO + O$	84·5	+ 6·05	
Magnesia	$Mg + O + H_2O$	29	+ 74·9	
	$Mg + H_2 + O_2$	29	+ 109·4	
Alumina	$Al_2 + O_3 + 3H_2O$	78·4	+ 195·8 or + 65·3 × 3	
Manganese protoxide	$Mn + O$	35·5	+ 47·4	
„ dioxide	$Mn + O_2$	43·5	+ 58·1	
Permanganic acid	$Mn_2 + O_7 + H_2O$ (hydrated)	120	...	+ 89
Chromic acid	$Cr_2O_3 + O_3$	103	+ 3·1	+ 4·2 or + 1·4 × 3
Iron protoxide	$Fe + O$	36	+ 34·5	
Iron peroxide	$Fe_2 + O_3$	80	+ 95·6 or + 31·9 × 3	
Iron (magnetic) oxide	$Fe_3 + O_4$	116	+ 134·5 or + 33·6 × 4	
	$FeO + Fe_2O_3$	...	+ 4·5	
Auric oxide	$Au_2 + O_3$	221	− 5·6	
Zinc oxide (anhydrous)	$Zn + O$	40·5	+ 43·2	
„ (hydrous)	$Zn + O + H_2O$	49·5	+ 41·8	
Cadmium oxide	$Cd + O$	64·0	+ 33·2	
Lead oxide (anhydrous)	$Pb + O$	111·5	+ 25·5	
„ (hydrous)	$Pb + O + H_2O$	120·5	+ 26·7	
Cuprous oxide	$Cu_2 + O$	71·4	+ 21·0	
Cupric oxide (anhydrous)	$Cu + O$	39·7	+ 19·2	
„ (hydrous)	$Cu + O + H_2O$	48·7	+ 19·0	
Stannous oxide	$Sn + O$	67	+ 34·9	
Stannic oxide	$Sn + O_2$	75	+ 67·9	
Mercurous oxide	$Hg_2 + O$	208	+ 21·1	
Mercuric oxide	$Hg + O$	108	+ 15·5	
Silver oxide	$Ag_2 + O$	116	+ 3·5[2]	
„ sesquioxide	$Ag_4 + O_3$	240	+ 10·5	
Bismuth oxide	$Bi + O_3$	234	+ 68·3	
Antimonious oxide	$Sb + O_3$	146	+ 88·7	
Antimonic oxide	$Sb + O_5$	162	+ 114·9	

[1] The heats of solution of the alkalis are by Berthelot. Without modifying the experimental bases of Thomsen, his calculations in Tables X. and XI. have been corrected by the small amounts necessary to put them in accord with the other data of the present Tables, such as the heat of formation of water, + 34·5 instead of + 34·7.

[2] Corrected by Berthelot.

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TABLE VIII.—HALOID SALTS.

Names.	Components.	Equivalents.	Heat disengaged.		Authorities.
			Solid Salt.	Dissolved Salt.	
Potassium chloride .	K + Cl	74·6	+ 105·0	+ 100·8	T.
Sodium chloride .	Na + Cl	58·5	+ 97·3	+ 96·2	T.
Ammonium chloride .	$N + H_4 + Cl$	53·5	+ 76·7	+ 72·7	B.
Strontium chloride .	$Sr + Cl_2$	79·3	+ 92·3	+ 97·8	T.
Barium chloride .	$Ba + Cl_2$	104·0	x + 31·7	x + 32·7	B.
			Br	Br	
			Gas. | Liquid	Gas. | Liquid.	
Potassium bromide .	K + Br	119·1	+ 100·4 | + 96·4	+ 95·0 | + 91·0	T.
			I	I	
Potassium iodide .	K + I	166·1	+ 85·4 | + 80·0	+ 80·1 | + 74·7	T.

TABLE IX.—FORMATION OF METALLIC SULPHIDES.[1]

Name.	Components.	Equivalents.	Heat disengaged, the body being		Authorities.
			Solid.	Dissolved.	
Potassium sulphide . .	$K_2 + S$	55·1	+ 51·1	+ 56·2	T. Sab.
Potassium polysulphide	$K_2S + S_2$	103·1	+ 6·2	+ 2·6[2]	Sab.
Potassium sulphydrate .	$K_2S + H_2S$	72·1	+ 9·2	+ 2·9[2]	Sab.
Sodium sulphide . .	$Na_2 + S$	39	+ 44·2	+ 51·6	T. Sab.
Sodium polysulphide .	$Na_2S + S_2$	87	+ 5·1	+ 2·5[2]	Sab.
Sodium sulphydrate .	$Na_2S + H_2S$	56	+ 9·3	+ 3·9[2]	Sab.
Ammonium sulphide .	$N_2 + H_8 + S$	34		+ 28·4	B.
Ammonium sulphydrate	$(NH_4)_2S + H_2S$	51		+ 3·0[2]	B.
Ammonium sulphydrate	$N_2 + H_{10} + S_2$ solid	51	+ 39·8	+ 36·6	B.
Strontium sulphide .	Sr + S	59·8	+ 47·6	+ 53·0	Sab.
Calcium sulphide . .	Ca + S	36	+ 46·0	+ 49·0	Sab.
Barium sulphide . .	Ba + S	84·5	x − 15·6		Sab.
Iron sulphide . . .	Fe + S	44	+ 11·9		B.
Zinc sulphide . . .	Zn + S	48·5	+ 21·5		B.
Lead sulphide . . .	Pb + S	119·5	+ 8·9		B.
Copper sulphide . .	$Cu_2 + S$	79	+ 10·1		T.
Copper sulphide . .	Cu + S	47·5	+ 5·1		T.
Mercury sulphide . .	Hg + S	116	+ 9·9		B.
Silver sulphide . . .	$Ag_2 + S$	124	+ 1·5		B.

[1] These numbers refer to solid sulphur; when the sulphur is gaseous, about 448°, it is necessary to add + 1·2. Towards 1000° the correction would be much larger, but it is not known with certainty.

[2] Components dissolved.

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TABLE X.—FORMATION OF CYANOGEN COMPOUNDS ACCORDING TO BERTHELOT.

Names.	Components.	Compounds.	Equivalent of compounds.	Heat disengaged, the compound—			
				Gaseous.	Liquid.	Solid.	Dissolved.
Cyanogen	C (diamond) + N	CN	26	− 37·3	...	...	− 33·9
	$C_2 + N_2$	C_2N_2	52	− 74·5	...	...	− 67·7
Hydrocyanic acid	C (diamond) + N + H	CNH	27	− 29·5	− 23·8	...	− 23·4
	Cy gas + H	CyH	27	+ 7·8	+ 13·5	...	+ 13·1 + 10·5 Cy diss.
Cyanogen chloride	C (diamond) + N + Cl	CNCl	61·5	− 35·7	− 27·2		
	Cy + Cl	CyCl	61·5	+ 1·6	+ 9·9		
Ammonium hydrocyanide	C (diamond) + N_2 + H_4	$CNHNH_2$	44	...	...	+ 3·2	− 1·2
	Cy + N + H_4	$CyNH_4$	44	...	...	+ 40·5	+ 36·1
Potassium cyanide	C (diamond) + N + K	CNK	65·1	...	...	+ 30·3	+ 27·4
	Cy + K	CyK	65·1	...	...	+ 67·6	+ 64·7
Sodium cyanide	Cy + Na	CyNa	49	...	...	+ 60·4	+ 59·9
Mercury cyanide	C_2 (diamond) + N_2 + Hg	C_2N_2Hg	126	...	...	− 25·4	− 26·9
	Cy_2 + Hg	Cy_2Hg	126	...	...	+ 11·9	+ 10·4
Potassium cyanate	C (diamond) + N + K + O	CNKO	81·1	...	...	+ 102·0	+ 96·8
	CyK + O	CyKO	81·1	...	...	+ 72·0	+ 69·7
Sulphocyanic acid	Cy + S + H	CySH	59	...	...	...	+ 19·9
K sulphocyanate	Cy + S + K	CySK	97·1	...	...	+ 87·8	+ 81·7
Na „	Cy + S + Na	CySNa	81	...	...	...	+ 77·1
Am „	Cy + S + N + H_4	CySAm	76	...	...	+ 59·1	+ 53·4
Hg „	Cy_2 + S_2 + Hg	Cy_2S_2Hg	158	...	...	+ 18·0	
Hydroferrocyanic acid	6HCy diss. + FeO pp Fe + H_4 + Cy_6	Cy_6FeH_4	108	...	...	+ 53·4	+ 53·6 + 39·3
Potassium ferrocyanide	6HCy diss. + $2K_2O$ diss. + FeO pp Fe + K_4 + Cy_6	Cy_6FeK_4	184·2	...	...	+ 182·6	+ 185·3 KCy diss.

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TABLE XI. — FORMATION OF THE PRINCIPAL SOLID OXYSALTS, FROM THEIR ELEMENTS TAKEN IN THEIR ACTUAL STATE.

Names.	Elements.	Equivalents.	Heat disengaged.
Nitrates	$N + O_3 + K$	101·1	+ 118·7
	$N + O_3 + Na$	85	+ 110·6
	$N_2 + O_3 + H_4$	80	+ 87·9
	$N_2 + O_6 + Sr$	103·8	+ 109·8
	$N_2 + O_6 + Ca$	82	+ 101·2
	$N_2 + O_6 + Pb$	165·5	+ 52·8
	$N + O_3 + Ag$	170	+ 28·7
Sulphates	$S + O_4 + K_2$	87·1	+ 171·1
	$S + O_4 + Na_2$	71	+ 163·2
	$S + O_4 + H_8 + N_2$	66	+ 141·1
	$S + O_4 + Sr$	91·8	+ 164·7
	$S + O_4 + Ca$	68	+ 160·0
	$S + O_4 + Mg$	60	+ 150·6
	$S + O_4 + Mn$	75·5	+ 123·8
	$S + O_4 + Pb$	151·5	+ 107·0
	$S + O_4 + Zn$	80·5	+ 114·4
	$S + O_4 + Cu$	79·7	+ 90·2
	$S + O_4 + Ag_2$	156	+ 82·9
Bisulphate	$S_2 + O_7 + K_2$	127·1	+ 236·0
Dithionate	$S_2 + O_6 + K_2$	119·1	+ 205·7
Sulphite	$S + O_3 + K_2$	79·1	+ 136·3
Bisulphite	$S_2 + O_5 + K_2$	111·1	+ 184·6
Hyposulphite	$S_2 + O_3 + K_2$	95·1	+ 133·4
Chlorates	$Cl + O_3 + K$	122·6	+ 94·6
	$KCl + O_3$	...	− 11·0
	$Cl + O_3 + Na$	106·5	+ 85·4
	$NaCl + O_3$	...	− 12·3
	$BaCl_2 + O_6$	152·1	− 12·6
Bromate	Br. gas $+ O_3 + K$	167·1	+ 87·6
	$KBr + O_3$	...	− 11·1
Iodate	I gas $+ O_3 + K$	214·1	+ 128·4
	$KI + O_3$	...	+ 44·1
Perchlorates	$Cl + O_4 + K$	138·6	+ 112·5
	$KCl + O_4$	138·6	+ 7·5
	$Cl + O_4 + Na$	122·1	+ 110·2
	$NaCl + O_4$	...	+ 3·0
	$BaCl_2 + O_8$	168·1	+ 1·1
	$Cl + O_4 + N + H_4$	117·5	+ 79·7
Phosphates	$P + O_4 + Na_3$	164	+ 451·6
	$P_2 + O_8 + Ca_3$	155	+ 460·6
Carbonates (carbon diamond)	$C + O_3 + K_2$	69·1	+ 138·9
	$C + O_3 + Na_2$	53	+ 135·1
	$C + O_3 + Sr$	73·8	+ 139·4
	$C + O_3 + Ca$	50	+ 134·7
	$C + O_3 + Mg$	42	+ 133·8
	$C + O_3 + Mn$	57·5	+ 104·0
	$C + O_3 + Pb$	133·5	+ 83·2
	$C + O_3 + Zn$	62·5	+ 97·1
	$C + O_3 + Ag_2$	138	+ 60·2
Bicarbonates	$C + O_3 + K + H$	100·1	+ 232·8
	$C + O_3 + Na + H$	84	+ 227·0
	$C + O_3 + N + H_4$	79	+ 205·6
Formiates (carbon diamond)	$C + H + K + O_2$	84·1	+ 154·8
	$C + H + Na + O_2$	68	+ 149·6
Acetates (carbon diamond)	$C_2 + H_3 + K + O_2$	98·1	+ 184·9
	$C_2 + H_3 + Na + O_2$	82	+ 179·2
	$C_2 + H_7 + N + O_2$	77	+ 159·6

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FORMATION OF THE PRINCIPAL SOLID OXYSALTS, ACCORDING TO THEIR ELEMENTS TAKEN IN THEIR ACTUAL STATE.—(*Continued.*)

Names.	Elements.	Equivalents.	Heat disengaged.
Oxalates (carbon diamond) .	$C_2 + K_2 + O_4$	166·2	+ 323·6 or 161·8 × 2
	$C_2 + Na_2 + O_4$	134	+ 313·8 or 156·9 × 2
	$C_2 + H_2 + N_2 + O_4$	124	+ 272·4 or 136·5 × 2
	$C_2 + Ag_2 + O_4$	304	+ 158·5 or 79·2 × 2
Chromates	Cr_2O_3 pp. $+ O_3 + K_2$	194·2	+ 206·7
	CrO_3 pp. $+ O + Na_2$	162	+ 190·3
Bichromates	$2(CrO_3)$ pp. $+ O + K_2$	147·1	+ 115·5
	$2(CrO_3)$ pp. $+ O + N_2 + H_2$	126	+ 85·4
	ACID SALTS.		
Bisulphates	$SO_3 + K_2SO_4 = K_2S_2O_7$	127·1	+ 13·1
	H_2SO_4 sol $+ K_2SO_4 =$ $2KHSO_4$	136·1	+ 7·5
	H_2SO_4 sol $+ Na_2SO_4 =$ $2NaHSO_4$	120·0	+ 8·1
Bichromate	$CrO_3 + K_2CrO_4$	147·1	+ 1·9
	HYDRATES.		
Hydrates	$K_2O + H_2O$	56·1	+ 21·2
	$Na_2O + H_2O$	40	+ 17·8
	$BaO + H_2O$	85·6	+ 8·8
	$SrO + H_2O$	60·8	+ 8·6
	$CrO + H_2O$	37	+ 7·55

TABLE XII.—HEAT DISENGAGED BY THE COMBUSTION OF ANY BODY WHATEVER BY MEANS OF VARIOUS OXIDISING AGENTS.

Name of Oxidising Agent.	Formulæ.	Equivalents.	Heat disengaged.
Free oxygen	$\frac{1}{8}O$	8	A Calories
Copper oxide	$\frac{1}{8}CuO$	39·7	A − 19·2
Lead oxide	$\frac{1}{8}PbO$	111·5	A − 25·5
Stannous oxide	$\frac{1}{8}SnO$	67	A − 34·9
Stannic oxide	$\frac{1}{8}SnO_2$	37·5	A − 34·0
Antimony oxide	$\frac{1}{8}SbO_2$	38·1	A − 31·1
Mercury oxide	$\frac{1}{8}HgO$	108	A − 15·5
Bismuth oxide	$\frac{1}{8}Bi_2O_3$	78	A − 23·0
Silver oxide	$\frac{1}{8}Ag_2O$	116	A − 3·5
Nitrogen monoxide . . .	$\frac{1}{8}N_2O$	22	A + 10·3
Nitric oxide	$\frac{1}{8}NO$	15	A + 10·8
Nitric peroxide (liquid) . .	$\frac{1}{8}N_2O_4$	11·5	A − 0·4
Nitric acid (liquid) . . .	$\frac{1}{8}HNO_3$	12·6	A − 1·4
Potassium nitrate . . .	$\frac{1}{8}KNO_3$	20·2	A − 5·4 or A − 2·5
Sodium nitrate	$\frac{1}{8}NaNO_3$	17	A − 4·4 or A − 2·3
Strontium nitrate . . .	$\frac{1}{16}Sr(NO_3)_2$	21·2	A − 5·4
Barium nitrate	$\frac{1}{16}Ba(NO_3)_2$	26·1	A − 5·5
Lead nitrate	$\frac{1}{16}Pb(NO_3)_2$	28·9	A − 8·8
Silver nitrate	$\frac{1}{8}AgNO_3$	34	A − 4·8
Ammonium nitrate . . .	$\frac{1}{8}NH_4NO_3$	40	A + 25·0
Potassium chlorate . . .	$\frac{1}{8}KClO_3$	20·4	A + 1·8
Potassium perchlorate . .	$\frac{1}{8}KClO_4$	17·3	A − 0·9
Manganese dioxide . . .	$\frac{1}{8}MnO_2$	43·5	A − 10·7
Potassium bichromate . .	$\frac{1}{8}K_2Cr_2O_7$	49·1	A − 7·9

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TABLE XIII.—MULTIPLE DECOMPOSITIONS OF AN EXPLOSIVE COMPOUND, BY M. BERTHELOT.

NH_4NO_3 solid[1] =

	Water.	
	Liquid.	Gaseous.
$N_2O + 2H_2O$	+ 29·5	+ 10·2
$N_2 + O + 2H_2O$	+ 50·1	+ 30·7
$N + NO + 2H_2O$	+ 28·5	+ 9·2
$\frac{1}{2}(N_2 + N_2O_3 + 6H_2O)$	...	+ 23·3
$\frac{1}{4}(3N_2 + N_2O_4 + 8H_2O)$	+ 48·8	+ 29·5
$\frac{1}{8}(2HNO_3 + 4N_2 + 9H_2O)$	+ 52·7	+ 33·4
$HNO_3 + NH_3$ (both gaseous)	...	− 41·3

TABLE XIV.—FORMATION OF THE PRINCIPAL SALTS IN THE DISSOLVED OR PRECIPITATED STATE BY MEANS OF DISSOLVED ACIDS (ONE EQUIVALENT DISSOLVED IN TWO OR FOUR LITRES OF LIQUID) AT 15°, ACCORDING TO BERTHELOT AND THOMSEN.

Bases.	Chlorides HCl 1 eq. = 2 lit.	Nitrates HNO_3 1 eq. = 2 lit.	Acetates $C_2H_4O_2$ 1 eq. = 2 lit.	Formates CH_2O_2 1 eq. = 2 lit.	Oxalates $\frac{1}{2}C_2H_2O_4$ 1 eq. = 2 lit.	Sulphates H_2SO_4 1 eq. = 2 lit.	Sulphides H_2S 1 eq. = 8 lit.	Cyanides HCy 1 eq. = 2 lit.	Carbonates CO_2 1 eq. = 16 lit.
Na_2O [2]	13·7	13·7	13·3	13·4	14·3	15·85	3·85	2·9	10·2
K_2O .	13·7	13·8	13·3	13·4	14·3	15·7	3·85	3·0	10·1
NH_3 .	12·45	12·5	12·0	11·9	41·7	14·5	3·1	1·3	5·3
CaO [3]	14·0	13·9	13·4	13·5	18·5	15·6	3·9	3·2	9·8
BaO [4]	13·85	13·9	13·4	13·5	16·7	18·4	...	3·2	11·1
SrO [5]	14·0	13·9	13·3	13·5	17·6	15·4	...	3·1	10·5
MgO [6]	13·8 [6]	13·8	...	...	...	15·6	...	...	9·0
MnO [6]	11·8	11·7	11·3	10·7	14·3	13·5	5·1	...	6·8
FeO .	10·7	...	9·9	...	...	12·5	7·3	...	5·0
NiO .	11·3	...	...	...	...	13·1	...	...	...
CoO .	10·6	...	...	...	...	13·3	...	7·2	...
CdO .	10·1	10·1	...	...	...	11·9	...	7·3	...
ZnO .	9·8	9·8	8·9	9·1	12·5	11·7	9·6	...	5·5
PbO .	7·7 [6]	7·7	6·5	6·6	12·8	10·7	13·3	...	6·7
„ .	10·7 [7]	...	...	...	...	...	...	...	...
CuO .	7·5	7·5	6·2	6·6	...	9·2	15·8	...	2·4
HgO .	9·45 [10]	...	3·0	...	7·0	...	24·35	15·5	...
Ag_2O .	20·1 [11]	5·2	4·7	...	12·9	7·2	27·9	20·9	6·9
$\frac{1}{2}Al_2O_3$	9·3	...	...	...	...	10·5	...	...	...
$\frac{1}{2}Fe_2O_3$.	5·9	5·9	4·5	...	...	5·7	...	...	...
$\frac{1}{3}Cr_2O_3$.	6·9	...	...	...	...	8·2	...	...	...

[1] If the salt were fused the numbers should be increased by about + 4.
[2] 1 eq. = 2 litres. [3] 1 eq. = 25 litres.
[4] 1 eq. = 6 litres. [5] 1 eq. = 10 litres.
[6] Precipitated, this applies to the earthy and metallic oxalates and carbonates as well as to the metallic oxides and sulphides. [7] Crystallized.
[8] 1 eq. = 4 litres; this applies to all salts formed by insoluble oxides.
[9] Very dilute.
[10] $HgCl_2$ — solid; + 11·0; HBr dilute: $HgBr_2$ — dissolved; + 13·7; solid + 15·4; HI dilute; HgI_2 red; + 23·2.
[11] HBr dilute and Ag_2O; + 22·5 to 25·5. HI dilute + Ag_2O; 26·5 at first, afterwards + 32·1.

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TABLE XV.—HEAT DISENGAGED IN THE FORMATION OF ORGANIC COMPOUNDS FROM THEIR ELEMENTS—CARBON DIAMOND; HYDROGEN, OXYGEN, AND NITROGEN, GASEOUS.

Names.	Components.	Molecular Weights.	Heat disengaged, the compound being				Authorities.	Heat of combustion at constant pressure (actual state).[1]
			Gaseous.	Liquid.	Solid.	Dissolved.		
HYDROCARBONS.								
Amorphous carbon changed into diamond	C	12	..	..	+ 3·0	..	F. & S.	97
Carbonic oxide	C + O	28	+ 25·8	..	..	..	B.	68·2
Carbonic acid	C + O_2	44	+ 94·0	..	+ 100·1	+ 99·6	F. & S.	..
Acetylene	C_2 + H_2	26	− 61·1	..	..	..	[B.] & T.	318·1
Ethylene	C_2 + H_4	28	− 15·4	..	..	..	[B.] D. F. & S. A. T.	341·4
Ethane	C_2 + H_6	30	+ 5·7	..	..	..	[B.] T.	389·3
Methane	C + H_4	16	+ 18·5	..	..	..	B. D. F. & S. A. T.	213·5
Amylene	C_5 + H_{10}	70	+ 5·4	+ 10·6	..	..	F. & S.	804·4
Diamylene	$2C_5$ + H_{10}	140	+ 26·1	+ 33·0	..	..	B.	1597
Benzene	C_6 + H_6	78	− 12·0	− 5·0	− 2·7	..	[B.] T.	776
Dipropargyl	$2(C_3$ + $H_3)$	78	− 82·8	..	..	..	B. & Og.	853·6 (gas)
Naphthalene	C_{10} + H_8	128	..	..	− 42·0	− 37·4	Rech.	1258
Terebenthene (liquid)	C_{10} + H_{16}	136	+ 8·6	+ 17·0	..	..	F. & S. D.	1475
Anthracene	C_{14} + H_{10}	178	..	..	− 115·0	..	Rech.	1776
ALCOHOLS.								
Methyl alcohol	C + H_4 + O	32	+ 53·6	+ 62·0	..	+ 64·0	F. & S.	170
Ethyl alcohol	C_2 + H_6 + O	46	+ 60·7	+ 70·5	..	+ 73·0	[B] D. A. F. & S.	324·5
Phenol	C_6 + H_6 + O	94	..	+ 34·0	+ 36·3	+ 32·0	F. & S.	737
Glycol	C_2 + H_6 + O_2	62	..	+ 111·7	..	+ 113·4	L.	283
Glycerin	C_3 + H_8 + O_3	92	..	+ 165·5	+ 169·4	+ 164·0	L.	392·5
Mannite and dulcite	C_6 + H_{14} + O_6	182	..	..	+ 290·0	+ 285·0 (mannite)	Rech.	763 to 760
Glucose and isomers	C_6 + H_{12} + O_6	180	..	..	+ 269·0	+ 167·0 (glucose)	Rech.	709 to 701
Ether	C_4 + H_{10} + O	74	+ 65·3	+ 72·0	..	+ 78	[B.] D. F. & S.	649
Polyglucosides (saccharose, starch, cellulose, etc.)	n(C_6 + H_{12} + O_6) − mH_2O	180n − 18m	..	..	+ 269n − 69m	(Approximately)	Rech.	n × (709 to 726)
Aldehyde	C_2 + H_4 + O	44	+ 50·5	+ 56·5	..	+ 60·1	B. & Og.	269·5
Acetone	C_3 + H_6 + O	58	+ 57·5	+ 65·0	..	+ 67·5	F. & S.	424

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ACIDS.								
Formic acid	$C + H_2 + O_2$	46	+ 88·2	+ 93·0	+ 95·5	+ 93·1	B.	70 (liquid)
Acetic acid	$C_2 + H_4 + O_2$	60	+ 121·5	+ 126·6	+ 129·1	+ 127·0	B.	199·4 (liquid)
Margaric acid	$C_{16} + H_{32} + O_2$	256	..	..	+ 233·0	..	F. & S.	2385
Stearic acid	$C_{18} + H_{36} + O_2$	284	..	..	+ 126·0	..	Rech.	2808 (2759 F. & S.)
Benzoic acid	$C_7 + H_6 + O_2$	122	..	..	+ 54·0	+ 47·5	Rech.	811
Oxalic acid	$C_2 + H_2 + O_4$	90	..	..	+ 197·0	+ 194·7	B. Rech.	60
Tartaric acid	$C_4 + H_6 + O_6$	150	..	..	+ 372·0	+ 368·7	Rech.	211
ETHERS.								
Compound ethers formed by organic acids	Acid + alcohol − water		..	Approximately equal to heat disengaged in the formation of the acid + heat of formation of the alcohol − heat of formation of water − 2·0 for each equivalent of alcohol	..	..	B.	Sum of the heats of combustion of the acid and of the alcohol + 2·0 approximately
Triolein	$C_{57} + H_{104} + O_6$	884	..	+ 228·0	..	..	D.	8718
Nitric ether	$C_2 + H_5 + N + O_3$	91	..	+ 49·3	..	+ 50·3	B.	311
Nitroglycerin	$C_3 + H_5 + N_3 + O_9$	227	..	+ 98	..	..	B.	356·5
Nitromannite	$C_6 + H_8 + N_6 + O_{18}$	432	..	..	+ 149·0	..	Sa. & Vie.	691
NITRO COMPOUNDS.								
Oxamide (solid)	$C_2 + H_4 + N_2 + O_2$	88	..	..	+ 140·0	..	B.	286
Mercury fulminate	$C_2 + N_2 + O_2 + Hg$	284	..	..	+ 62·9	..	B. & Vie.	250·9 (Hg free)
Gun-cotton	$C_{24} + H_{29} + N_{11} + O_{42}$	1143	..	..	+ 624·0	..	Sa. & Vie.	633
Collodion cotton	$C_{24} + H_{31} + N_9 + O_{38}$	1053	..	..	+ 696·0	..	B.	2629·5
Nitrobenzene	$C_6 + H_5 + N + O_2$	123	..	+ 4·2	+ 6·9	..	B.	732
Dinitrobenzene	$C_6 + H_4 + N_2 + O_4$	168	..	..	+ 12·7	..	B.	689
Picric acid	$C_6 + H_3 + N_3 + O_7$	229	..	..	+ 49·1	+ 41·0	Sa. & Vie.	618·4
Potassium picrate	$C_6 + H_2 + K + N_3 + O_7$	267	..	..	+ 117·5	+ 107·5	Sa. & Vie.	619·7 (Bicarb. K)
Ammonium picrate	$C_6 + H_6 + N_4 + O_7$	246	..	..	+ 80·1	+ 71·4	Sa. & Vie.	690·9
Cyanogen	$C_2 + N_2$	52	− 74·5	..	..	− 67·7	B.	262·5
Hydrocyanic acid	$C + N + H$	27	− 29·5	− 23·8	..	− 23·4	B.	158 (Cy gas)
Diazobenzene nitrate	$C_6 + H_5 + N_3 + O_3$	167	..	..	− 47·4	..	B. & Vie.	782·9

[1] The heats of combustion are known within about one or two hundredths. The heats of formation, which are deduced from them, have a probable error equal to the value of this approximation referred to the absolute value of the heat of combustion. It is admitted, C diamond + O_2 = CO_2 + 94·0.

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TABLE XVI.—FORMATION OF ALDEHYDES AND ORGANIC ACIDS BY OXIDATION.

Names.	Components.	Compounds.	Heat disengaged.	Physical state of the Compounds.
	1. WITH THE HYDROCARBONS.			
Ethylic aldehyde	$C_2H_4 + O$	C_2H_4O	+ 65·9	Gas
			+ 71·9	Liquid
Ortho-propylic aldehyde	$C_3H_6 + O$	C_3H_6O	+ 87·3	Liquid
Iso-propylic aldehyde			+ 83·3	Liquid
			+ 133·2	Gas, liquid
Acetic acid	$C_2H_4 + O_2$	$C_2H_4O_2$	+ 138·3	Solid
			+ 133·9	Solid
Propionic acid	$C_3H_6 + O_2$	$C_3H_6O_2$	+ 153·3	Liquid
Oxalic acid	$C_2H_2 + O_4$	$C_2H_2O_4$	+ 258·0	Solid
Acetic acid	$C_2H_2 + O + H_2O$	$C_2H_4O_2$	+ 118·7	Liquid
			+ 121·2	Solid
			+ 128·9	Gas
Formic acid	$CH_4 + O_2$	$CH_2O_2 + H_2O$	+ 143·5	Liquid
			+ 147·3	Solid
	2. WITH ALDEHYDES.			
Acetic acid	$C_2H_4O + O$	$C_2H_4O_2$	+ 67·8	Both bodies gaseous
			+ 66·4	Actual state
Propionic acid	$C_3H_6O + O$	$C_3H_6O_2$	+ 74·0	Actual state
	3. WITH ALCOHOLS.			
Liquid formic acid	$CH_2O + O_2$	$CH_2O_2 + H_2O$	+ 100·0	Actual state
Liquid acetic acid	$C_2H_6O + O_2$	$C_2H_4O_2 + H_2O$	+ 125·1	Actual state
Liquid valerianic acid	$C_5H_{12}O + O_2$	$C_5H_{10}O_2 + H_2O$	+ 131·0	Actual state
Solid margaric acid	$C_{16}H_{34}O + O_2$	$C_{16}H_{32}O_2 + H_2O$	+ 180·0	Actual state
Solid oxalic acid	$C_2H_6O + O_5$	$C_2H_2O_4 + 2H_2O$	+ 261·0	Actual state
	$C_2H_4O_2 + O_2$	$C_2H_2O_4 + H_2O$	+ 139·4	Actual state

TABLE XVII.—VARIOUS ORGANIC COMPOUNDS.

Names.	Components.	Compounds.	Equivalents.	Heat disengaged.
	FORMATION OF AMIDES BY AMMONIACAL SALTS.			
Formic amide	CH_2O_2, NH_3 diss.	CH_3NO (diss.)	45	− 1·0
Formic nitril or hydro-cyanic acid	CH_2O_2, NH_3 diss.	HCN (diss.)	27	− 10·4
Oxamide	$C_2H_2O_4$, $2NH_3$ cryst.	$C_2H_4N_2O_2$ (solid)	88	− 1·2 × 2
	FORMATION OF ISOMERIC AND POLYMERIC BODIES.			
Diamylene	$2C_5H_{10}$ liquid	$C_{10}H_{20}$ liquid	140	+ 11·8
	$2C_5H_{10}$ gaseous	$C_{10}H_{20}$ liquid	140	+ 22·3
	$2C_5H_{10}$ gaseous	$C_{10}H_{20}$ gaseous	140	+ 15·4
Benzene	$3C_2H_2$ (actual reaction)	C_6H_6 (gas)	78	+ 171·0
Dipropargyl	$3C_2H_2$ (theoretical action)	C_6H_6 (gas)	78	+ 100·5
	C_6H_6 (Benzene idem.)			− 70·5

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TABLE XVIII.—FORMATION OF NITRIC DERIVATIVES.

Organic compound + HNO_3 liquid = Nitric derivative + H_2O (liquid).

Names.	Compounds.	Equivalents.	Heat disengaged.
Nitric ether (B.)	$C_2H_4(HNO_3)$	91	+ 6·2
Nitroglycerin (B.)	$C_3H_23(HNO_3)$	227	+ 4·7 × 3
Nitromannite (B.)	$C_6H_26(HNO_3)$	453	+ 3·9 × 6
Gun-cotton (B.)	$C_{24}H_{12}O_911(HNO_3)$	1143	+ 11·4 × 11
Nitrobenzene (B.)	$C_6H_5(NO_2)$	123	+ 36·6
Dinitrobenzene (B.)	$C_6H_42(NO_2)$	168	+ 36·2 × 2
Picric acid (Sa. & Vie.)	$C_6H_23(NO_2)O$	229	+ 34·0 × 3
Chloronitrobenzene (B.)	$C_6H_4Cl(NO_2)$	157·5	+ 36·4
Nitrobenzoic acid (B.)	$C_7H_5(NO_2)O_2$	167	+ 36·6
Nitronaphthaline (Tr. & H.)	$C_{10}H_7(NO_2)$	173	+ 36·5
Nitrotoluene (Tr. & H.)	$C_7H_7(NO_2)$	137	+ 38·0

TABLE XIX.—HEAT OF FUSION OF ELEMENTS AND SOME OF THEIR COMPOUNDS.

Names.	Formulæ.	Equivalents.	Temperature of Fusion.	Heat of Fusion.	Authority.
			degrees.	C.	
Bromine	Br	80	− 7·3	− 0·13	R.
Iodine	I	127	+ 113·6	− 1·49	R.
Sulphur	S	16	+ 113·6	− 0·15	P.
Phosphorus	P	31	+ 44·2	− 0·15	P.
Mercury	Hg	100	− 39·5	− 0·28	P.
Lead	Pb	103·5	+ 335·0	− 0·53	P.
Bismuth	Bi	210	+ 265·0	− 2·6	P.
Tin	Sn	59	+ 235·0	− 0·84	P.
Gallium	Ga	35	+ 30·0	− 0·66	B.
Cadmium	Cd	56	+ 500·0	− 0·65	P.
Silver	Ag	108	+ 954·0	− 0·23	P.
Platinum	Pt	98·6	+ 1775·0	− 2·68	Vi.
Palladium	Pd	53	+ 1500·0	− 1·9	Vi.
Water	H_2O	9	+ 0·0	− 0·715	Ds.
Iodine chloride	ICl	162·5	+ 25·0	− 2·3	B.
Nitrogen pentoxide	N_2O_5	54	+ 29·5	− 4·14	B.
Nitric acid	HNO_3	63	− 47·0	− 0·6	B.
Sulphuric acid	H_2SO_4	49	+ 8·0	− 0·43	B.
Sulphuric acid (hydrate)	$H_2SO_4H_2O$	58	+ 8·8	− 1·84	B.
Naphthalen	$C_{10}H_8$	128	+ 79·0	− 4·6	Al.
Glycerin	$C_3H_8O_3$	92	+ 17·0	− 3·9	B.
Formic acid	CH_2O_2	46	+ 8·2	− 2·43	B.
Acetic acid	$C_2H_4O_2$	60	+ 17·0	− 2·5	B.
Benzene	C_6H_6	78	+ 4·5	− 2·27	Pett.
Nitrobenzene	$C_6H_5NO_2$	123	+ 3·0	− 2·74	Pett.
Phenol	C_6H_6O	94	+ 42·0	− 2·34	Pett.
Potassium nitrate	KNO_3	101	+ 333·5	− 5·5	P.
Sodium nitrate	$NaNO_3$	85	+ 306·0	− 4·9	P.

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TABLE XX.—HEAT OF VOLATILIZATION (LATENT HEAT) OF THE ELEMENTS AND THEIR PRINCIPAL COMPOUNDS, REFERRED TO THE SAME GASEOUS VOLUME (22·32 LITRES) UNDER ATMOSPHERIC PRESSURE.

Names.	Formulæ.	Molecular Weights.	Latent Heat.	Authorities.
Bromine (liquid)	Br_2	160	7·2	R.
Iodine (liquid)	I_2	254	6·0	F.
Sulphur (liquid)	S_2	64	4·6	F.
Mercury (liquid)	Hg	200	15·4	F.
Water	H_2O	18	9·65	R.
Ammonia	NH_3	17	4·4	R.
Hydrofluoric acid	HF	20	7·2	Guntz.
Nitrogen monoxide	N_2O	44	4·4	F.
Nitric peroxide	NO_2	46	4·3	B.
Nitrogen pentoxide (liquid)	N_2O_5	108	4·8	B.
Nitric acid	HNO_3	63	7·25	B.
Sulphurous anhydride	SO_2	64	6·2	F.
Sulphuric anhydride (solid)	SO_3	80	11·8	B.
Carbonic acid (solid)	CO_2	44	6·1	F.
Carbon disulphide	CS_2	76	6·4	R.
Hydrocyanic acid	HCN	27	5·7	B.
Cyanogen chloride	$CNCl$	61·5	8·3	B.
Amylene	C_5H_{10}	70	5·25	B.
Diamylene	$C_{10}H_{20}$	140	6·9	B.
Benzene	C_6H_6	78	7·2	R.
Terebenthene	$C_{10}H_{16}$	136	9·4	R.
Methyl alcohol	$CH_2(H_2O)$	32	8·45	R.
Ethyl alcohol	$C_2H_4(H_2O)$	46	9·8	R.
Aldehyde	C_2H_4O	44	6·0	B.
Acetone	C_3H_6O	58	7·5	R.
Formic acid	CH_2O_2	46	4·8	B. & Og.
Acetic acid	$C_2H_4O_2$	60	5·1	B. & Og.
Ethyl acetate	$C_2H_4(C_2H_4O_2)$	88	10·9	R.
Ordinary ether	$C_2H_4(C_2H_6O)$	74	6·7	R.

The calculation of the pressures exerted at the moment of decomposition of an explosive substance, requires not only the knowledge of the heat disengaged by the transformation, but also that of the specific heat of the products of the explosion and their volume. It is equally necessary to know the specific heat of the component bodies, in order to know the effects of a certain heating on these bodies. Finally, the volume which they occupy for a given weight, and which is deduced from their density, plays an essential part in the valuation of the density of charge and specific pressure (p. 28). These considerations have induced the author to give the following tables :—

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TABLE XXI.—SPECIFIC HEATS OF SUBSTANCES WHICH CAN BE OBSERVED IN THE STUDY OF EXPLOSIVES.—GASES.

Names.	Formulæ.	Molecular Weights.	Specific Heat at constant pressure, referred to 1 grm.	Specific Heat at constant pressure, referred to the molecular weight under volume 22·32 litres.
Hydrogen	H_2	2	3·410	6·82 [1]
Oxygen	O_2	32	0·217	6·96
Nitrogen	N_2	28	0·244	6·82
Chlorine	Cl_2	71	0·121 (0°–200°)	8·58
Carbonic oxide	CO	28	0·245	6·86
Nitric oxide	NO	30	0·232	6·96
Nitrogen monoxide	N_2O	44	0·226 (0°–200°)	9·94
Carbonic acid	CO_2	44	0·215 (0°–200°)	9·50
Sulphurous anhydride	SO_2	64	0·154 (0°–200°)	9·86
Water vapour	H_2O	18	0·480 (128°–220°)	8·64
Hydrochloric acid gas	HCl	36·5	0·185	6·75
Sulphuretted hydrogen gas	H_2S	34	0·243	8·30
Ammonia gas	NH_3	17	0·535 (0°–200°)	9·11
Methane	CH_4	16	0·593 (0°–200°)	9·50
Ethylene	C_2H_4	28	0·404 (0°–200°)	11·30

[1] These numbers represent small calories. The specific heats at constant volume are deduced from these by subtracting the constant 2.

TABLE XXII.—SPECIFIC HEATS OF SUBSTANCES WHICH CAN BE OBSERVED IN THE STUDY OF EXPLOSIVES.—SOLIDS AND LIQUIDS.

Names.	Formulæ.	Equivalents.	Specific Heats referred to 1 grm.	Specific Heats referred to the equivalent weight.
ELEMENTS.				
Sulphur	S	16	0·203 solid 0·234 liquid (120° to 150°)	3·2 3·7
Phosphorus	P	31	0·19 solid 0·20 liquid	5·9 6·3
Arsenic	As	75	0·081	6·1
Antimony	Sb	122	0·051	6·2
Bismuth	Bi	210	0·031	6·5
Tin	Sn	59	0·055	3·3
Carbon	C	12	0·202 graphite, coke 0·241 calcined wood	2·4 2·9
Iron	Fe	28	0·114	3·2
Zinc	Zn	32·5	0·096	3·1
Copper	Cu	31·5	0·095	3·0
Mercury	Hg	100	0·033	3·3
Lead	Pb	103·5	0·0314	3·3
Silver	Ag	108	0·334	6·2
Platinum	Pt	98·5	0·324	3·2
Gold	Au	98·5	0·324	3·2

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SPECIFIC HEATS OF SUBSTANCES WHICH CAN BE OBSERVED IN THE STUDY OF EXPLOSIVES—SOLIDS AND LIQUIDS.—(*Continued.*)

Names.	Formulæ.	Equivalents.	Specific Heats referred	
			to 1 grm.	to the equivalent weight.
OXIDES.				
Magnesia	MgO	20	0·244	5·9
Chromium oxide	Cr_2O_3	76	0·19	14·5
Alumina	Al_2O_3	51	0·217	11·2
Ferric oxide	Fe_2O_3	80	0·16	13·1
Zinc oxide	ZnO	40·5	0·13	5·4
Copper oxide	CuO	39·5	0·14	5·7
	Cu_2O	71	0·11	7·7
Lead oxide	PbO	111·5	0·051	5·7
Stannic oxide	SnO_2	75	0·093	14·0
Silica	SiO_2	60	0·195	11·4
CHLORIDES AND SULPHIDES.				
Ammonium chloride	NH_4Cl	53·5	0·373	20·0
Potassium chloride	KCl	74·6	0·173	12·9
Sodium chloride	$NaCl$	58·5	0·214	12·5
Barium chloride	$BaCl_2$	104·0	0·090	9·3
Calcium chloride	$CaCl_2$	55·5	0·164	9·2
Silver chloride	$AgCl$	143·5	0·091	13·1
Potassium sulphide	K_2S	55·1	...	8·9 [1]
Sodium sulphide	Na_2S	38·0	...	8·9 [1]
Iron sulphide	FeS	44·0	0·136	6·0
Potassium ferrocyanide	$K_4Fe_2Cy_6$	212·0	0·28	59·0
NITRATES.				
Potassium nitrate	KNO_3	1·01	0·239 solid 0·332 liquid	24·2 33·5
Sodium nitrate	$NaNO_3$	8·5	0·278	23·7
Barium nitrate	$Ba(NO_3)_2$	130·5	0·15	19·0
Strontium nitrate	$Sr(NO_3)_2$	105·8	0·18	19·1
Lead nitrate	$Pb(NO_3)_2$	165·5	0·11	18·2
Silver nitrate	$AgNO_3$	17·0	0·143	24·4
Ammonia nitrate	NH_4NO	80·0	0·455	36·4
SULPHATES AND CHROMATES.				
Potassium sulphate	K_2SO_4	87	0·190	16·6
Sodium sulphate	Na_2SO_4	71	0·229	16·2
Calcium sulphate	$CaSO_4$	68	0·18	12·7
Barium sulphate	$BaSO_4$	116·6	0·11	12·6
Strontium sulphate	$SrSO_4$	91·8	0·14	12·4
Magnesium sulphate	$MgSO_4$	60·0	0·22	13·3
Copper sulphate	$CuSO_4$	80·5	0·134	14·1
Potassium hyposulphite	$K_2S_2O_3$	95	0·20	18·7
Sodium hyposulphite	$Na_2S_2O_3$	79	0·221	17·5
Potassium chromate	K_2CrO_4	97	0·19	27·6
Potassium bichromate	$K_2Cr_2O_7$	147	0·187	18·2
Lead chromate	$PbCrO_4$	161	0·09	14·5
CARBONATES.				
Potassium carbonate	K_2CO_3	69·1	0·21	15·0
Sodium carbonate	Na_2CO_3	53·0	0·27	14·5
Calcium carbonate	$CaCO_3$	50·0	0·209	10·5
Barium carbonate	$BaCO_3$	98·5	0·11	10·7
Lead carbonate	$PbCO_3$	134·0	0·145	10·7

[1] Theoretical valuation.

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SPECIFIC HEATS OF SUBSTANCES WHICH CAN BE OBSERVED IN THE STUDY OF EXPLOSIVES—SOLIDS AND LIQUIDS.—(*Continued.*)

Names.	Formulæ.	Equivalents.	Specific Heats referred	
			to 1 grm.	to the equivalent weight.
CHLORATES.				
Potassium chlorate	$KClO_3$	122·6	0·21	25·7
Potassium perchlorate	$KClO_4$	138·6	0·19	26·3
WATER, ACIDS, ORGANIC COMPOUNDS.				
Water	H_2O	9	1·0 liquid 0·50 solid	9·0 4·5
Nitric acid	HNO_3	63	0·445 liquid	28·0
Sulphuric acid	H_2SO_4	49	0·34 liquid	16·7
Benzene	C_6H_6	78	0·44 liquid	34·0
Alcohol	C_2H_6O	46	0·595 about 20°	27·3
Glycerin	$C_3H_8O_3$	92	0·591	54·4
Mannite	$C_6H_{14}O_6$	182	0·324	59·1
Cane sugar	$C_{12}H_{22}O_{11}$	342	0·301	103·0

The specific heats of solid compounds can be approximately calculated from the sum of those of their elements; the latter being taken, not with the real values which they possess in the free state, but with the values calculated by Kopp from the mean of the observed values for their compounds. He has thus obtained the following empirical values referred to the equivalent weights:—

6·4 for K, Li, Na, Rb, Tl, Ag, As, Bi, Sb, Br, I, Cl.
5·4 for P.
5·0 for F.
3·8 for Si (28).
3·2 for Al, Au, Ba, Sr, Ca, Cd, Co, Cr, Cu, Fe, Hg, Ir, Mg, Mn, Ni, Os, Pb, Pd, Pt, R, Sn, Ti, Mo, N, Zn, Se, Te.
2·7 for S (16), B (11).
2·3 for H.
2·0 for O (8).
1·8 for C (12).

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TABLE XXIII.—DENSITIES AND MOLECULAR VOLUMES OF SOME BODIES.

Name.	Symbols.	Equivalents.	Density.	Molecular Volume.
				cub. cms.
Sulphur	S	16	2·04	7·9
Carbon	C	6	3·5 diamond 2·27 graphite 1·57 amorph.	1·7 2·7 3·8
Copper	Cu	31·6	8·94	3·5
Lead	Pb	103·5	11·4	9·1
Silver	Ag	108	10·47	10·3
Iron	Fe	28	7·8	3·6
Tin	Sn	59	7·3	8·1
Mercury	Hg	100	13·59	7·35
Zinc	Zn	32·5	6·9	4·7
Magnetic iron oxide	Fe_3O_4	116	5·9	23
Lead oxide	PbO	111·5	9·36	11·9
Tin oxide	SnO_2	75	6·71	11·2
Chromium oxide	Cr_2O_3	79	5·2	15
Alumina	Al_2O_3	51·5	3·5 to 4·1	15 to 12·5
Silica	SiO_2	60	2·65	23
Potassium chloride	KCl	74·6	1·94	38
Sodium chloride	NaCl	58·5	2·15	27
Barium chloride	$BaCl_2$	104·6	3·70	28
Strontium chloride	$SrCl_2$	79·3	2·80	28
Ammonium chloride	NH_4Cl	53·5	1·53	35
Potassium cyanide	KCN	65·1	1·52	43
Potassium nitrate	KNO_3	101·1	2·06	49
Sodium nitrate	$NaNO_3$	85	2·20	39
Barium nitrate	$Ba(NO_3)_2$	130·5	3·18	41
Lead nitrate	$Pb(NO_3)_2$	165·5	4·40	38
Silver nitrate	$AgNO_3$	170	4·35	39
Ammonium nitrate	NH_4NO_3	80	1·71	41
Potassium carbonate	K_2CO_3	69·1	2·26	31
Sodium carbonate	Na_2CO_3	53	2·46	21·5
Barium carbonate	$BaCO_3$	98·5	4·30	23
Strontium carbonate	$SrCO_3$	73·8	3·62	20
Calcium carbonate	$CaCO_3$	50	2·71	18
Potassium sulphate	K_2SO_4	87·1	2·66	33
Sodium sulphate	Na_2SO_4	71	2·63	27
Barium sulphate	$BaSO_4$	116·5	4·45	26
Strontium sulphate	$SrSO_4$	91·8	3·59	26
Calcium sulphate	$CaSO_4$	68	2·93	23
Potassium chlorate	$KClO_3$	122·6	2·33	52·6
Potassium bichromate	$K_2Cr_2O_7$	147	2·69	55
Cane sugar	$C_{12}H_{22}O_{11}$	342	1·59	215

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CHAPTER II.

CALORIMETRIC APPARATUS.

§ 1. General Remarks.

1. The author has carried out almost all the measurements of the quantities of heat liberated or absorbed in his experiments with the water calorimeter. It is very well adapted for determinations concerning explosive substances. This instrument, employed by Dulong and Regnault, and also by Thomsen, appears to offer the guarantees of the greatest accuracy. In fact, the quantities determined by it approach as closely as possible the theoretical definition of the "calorie"; whilst the ice calorimeter of Lavoisier and Laplace, as well as that of Bunsen, and the mercury calorimeter of Favre and Silbermann, determine different quantities, such as the weight of water liquefied, or the expansions of certain liquids. The relation of these quantities to the calorie must be found separately, by a system of special experiments, and it is liable to incessant variation, according to the conditions of the surrounding medium. In the use of these instruments, therefore, all the uncertainties of indirect measurements occur.

2. The conditions under which the calorimeter is employed are very simple, and capable of being easily reproduced by all chemists and physicists who desire to carry out similar experiments. The measurements are, moreover, more promptly executed, and the calculation easier than by any other method. For the complete discussion of the process, the verification of the thermometers, and the arrangements special to certain experiments, the reader is referred to the author's "Essai de Mécanique Chimique," where these subjects are more fully treated.

§ 2. Description of the Calorimeter.

1. The apparatus consists of three fundamental parts, viz. a calorimeter; a thermometer; an envelope. The annexed

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sketch will give a sufficient idea of the apparatus (scale one-fifth).

2. The calorimeter, properly so called, consists of a platinum, brass, or glass vessel, with very thin walls, goblet shaped, provided with various fittings, and placed on three cork points. We shall now describe it in detail.

In the greater number of the experiments, a cylindrical platinum vessel, capable of containing at least 600 cub. cms. of liquid, was used. It is 0·120 metre in height by 0·085 metre in

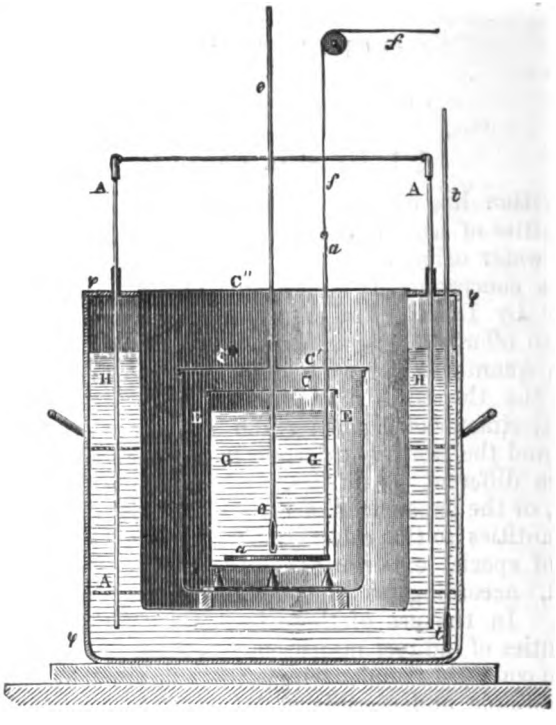

Fig. 19.—Berthelot's Calorimeter, with its Envelopes.

GG, calorimeter of platinum; C, the cover; θθ, calorimetric thermometer; EE, silver-plated envelope; C', cover of same; HH, double envelope of tin plate, filled with water; C'', cover of same; AAA, stirrer; tt, its thermometer; φφ, jacket of thick felt covering the tin plate envelope.

diameter, and weighs 63·43 grms. It is provided with a platinum cover, fixed with a bayonet joint on the edges of the cylindrical vessel, and pierced with various holes for the passage of the thermometer, stirrer, conducting tubes for the gases, liquids, etc. This cover weighs 12·18 grms.

It is only employed in certain experiments, the calorimeter being for the most part uncovered.

In experiments in which the equilibrium of temperature is

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almost instantaneous, the cover and the stirrer may be omitted, and the thermometer itself employed to agitate the liquid, which simplifies operations.

Under these conditions the calorimeter is very simple, as will be seen. Reduced to water it is equivalent to 3 grms. to 4 grms., according to the accessory pieces, that is to say, that its calorimetric mass does not exceed the two-hundredth part of the mass of the aqueous liquids which it contains, a circumstance which is very favourable to accuracy in experiments.

The author has also used several other platinum calorimeters, one with capacity of 1 litre, which has served for the greater number of his experiments on the detonation of gases, another of 2·5 litres.

In certain experiments where it was necessary that contact with the air should be completely avoided, glass phials containing 700 cms. to 800 cms. have been used as calorimeters, always placing them in the same protecting envelope. These instruments give measurements which are the more exact the larger they are, but on the condition of consuming larger weights of the substances. This limits the use of the large instruments. On the contrary, the small ones are more subject to corrections for cooling which may be neglected with calorimeters of half a litre and upwards, for the duration of an ordinary experiment (one to two minutes) and whenever the excesses of temperature remain less than 2°.

3. *Stirrer.*—In the experiments in which the stirring of the water by means of the thermometer was insufficient, or presented any difficulty, a stirrer of special form was employed, superior to those hitherto used, because it more completely mixes all the layers of water, with less expenditure of force.

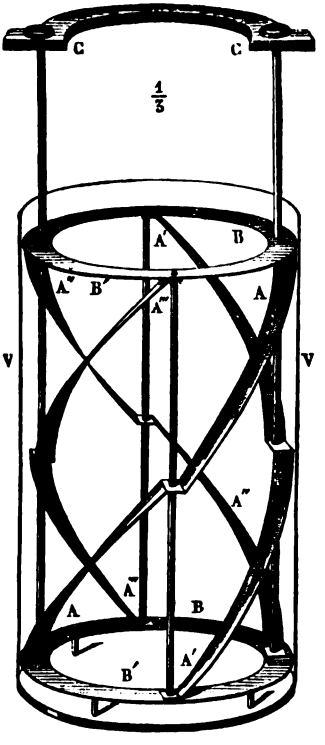

Fig. 20.

This stirrer (Fig. 20) consists of four wide helicoidal blades, A A′ A″ A‴ very thin, inclined at about 45° to the vertical and normal to the internal surface of the cylinder employed as a calorimeter. They are mounted on a frame formed of two

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horizontal rings, B B′, which hold the frame together at its ends, and of four strong vertical rods, the whole being in platinum or brass, as may be required.

The blades, about 0·010 metre in width, and the rings of equal breadth, are arranged so as to form a frame, concentric to an internal cylindrical space, the whole being in its turn enveloped and almost touched by the cylindrical vessel, V V, which constitutes the calorimeter.

Two of the vertical rods are prolonged about 0·15 metre above the calorimeter, and joined at their upper end by a half ring of wood, C C, of suitable width and thickness. The lower ring is provided with four small feet or prolongations, a few millimetres in length, and arranged so that the stirrer rests on their rounded ends, at the bottom of the calorimeter.

The whole may be seen, in the centre of the calorimeter (Fig. 20). In the cylindrical space surrounded by the stirrer are placed the thermometer and suitable apparatus.

In order to employ this stirrer, the half ring is held in the hand, or by some mechanical appliance (turn-spit, hydraulic, or electro-magnetic motor, etc.), the stirrer is lifted a few millimetres, and a horizontal and rotary movement around its vertical axis is imparted to it. This movement is alternating, and comprises an arc of from 30° to 35°. In consequence the water in the calorimeter is impelled towards the centre, and at all heights at the same time, being sharply thrust forward by the helicoidal blades, which strike the water at an angle of 45° with the vertical.

The degree of perfection which is hereby attained in the mixture of the layers, and the promptitude with which this result is obtained, even with a slight effort and slow movement, are surprising.

Besides, the stirrer not coming continually out of the liquid, as happens with stirrers moved up and down, is not exposed to the very sensible evaporation to which the latter give rise, nor to the causes of error which result therefrom.

4. The calorimeter just described may be employed under extremely varied conditions. A full account will be found in the "Essai de Mécanique Chimique" and in the author's "Mémoires." Some of the special instruments employed for effecting chemical reactions in the interior of this calorimeter will be described in the following chapters, in connection with the experiments for which they have been constructed.

§ 3. Detonator or Calorimetric Bomb.

1. A description will now be given of the apparatus used to measure by detonation both the heat of combustion of hydrocarbon gases, or by an inverse process the heat of formation of

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the oxygen yielding gases such as nitrogen monoxide and dioxide, the apparatus employed not having been described in the work previously quoted.

2. The method consists in mixing in a suitable vessel the gas or vapour with the proportion of oxygen strictly necessary to burn it completely, or even with a slight excess of oxygen when this excess is not detrimental; then, in causing the explosion of the mixture in a closed vessel, and at constant volume. The detonator having been previously placed in a calorimeter, the heat produced is measured. By proceeding in this manner, the combustion lasts only a fraction of a second, and is always total, at least for gases properly so called; in short, the calorimetric measurement is effected in the shortest possible time—that is to say, under the conditions of the greatest accuracy.

3. From this measurement is deduced, by calculation, the heat liberated by the total combustion of the gas, simple or compound. If, further, the sum of the quantities of heat liberated by the combustion of the elements, when the gas is compound, be known, it is sufficient to deduct from this sum the heat of combustion of the said compound gas to obtain the heat of formation of this gas, by means of its elements.

For example, marsh gas, CH_4, taken at the weight of 16 grms., liberates, when burning at constant pressure, 213·5 Cal. Now its elements liberate respectively, for C = 12 grms., taken in the diamond form, 94 Cal., and for H_4 = 4 grms., 138 Cal.; hence we conclude that the formation of marsh gas from its elements C (diamond) + H_4 = CH_4; liberates + 94 + 138 − 213·5 = + 18·5 Cal.

4. The same method has enabled the author to measure in an inverse sense the heat of formation of nitric oxide employed as oxygen yielding gas. This gas, mixed with hydrogen, does not detonate under the influence of the electric spark; but it explodes violently when mixed with ethylene or cyanogen. Such a mixture has, therefore, been made in the proportions strictly necessary for total combustion, exploded in the apparatus, and the heat liberated measured.

The same experiment has been made with the same combustible gases and pure oxygen.

This having been done, it is sufficient to deduct the heat liberated in the first case from that produced in the second, in order to obtain the heat of formation of nitric oxide by its elements without any other data than these two intervening in this calculation. In this way we find a negative number, viz. − 21·6 Cal. for N + O = NO (30 grms.), which means that the combustion of an oxidisable body, effected by nitric oxide, liberates more heat than the same combustion effected by pure oxygen.

Thus nitric oxide is formed from its elements with absorp-

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tion of heat, and contains more energy than the oxygen and nitrogen which constitute it. This circumstance is all-important, for it explains the combustion power of the oxygenated compounds of nitrogen.

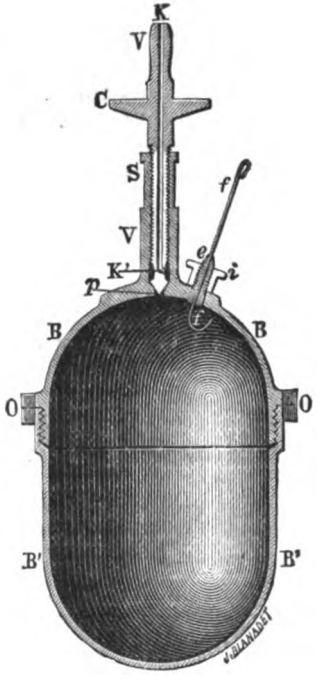

Fig. 21.—Calometric bomb (section).

5. This being established, we proceed to describe the apparatus employed, and to give some types of experiments in order to characterise the method. As for the forms of the apparatus, they belong to two models—the ellipsoidal and the semi-cylindrical bomb, the method of closing these two models being slightly different. But the introduction of the gases, their extraction, the ignition, and the measurement of the heat liberated are always effected in the same manner.

Fig. 21 represents the calorimetric bomb employed for the author's first measurements. Its capacity is 218 cms., and its value in water 51 grms.

It is formed of a receiver, B'B', and of a cover, BB (Fig. 22), held together by a screw joint provided with lugs, OO, both of steel plate, 2·5 mms. in thickness. They were electro-plated internally with a very thick layer of gold, weighing about 22 grms., which resisted all the explosions. At first the bomb was plated internally with platinum, but platinum thus deposited does not stand prolonged use. After a certain number of observations, the platinum is raised, or eliminated, during cleaning, and the exposed iron becomes oxidised during the explosions, especially when water is formed. Platinum electro-plating was therefore completely abandoned. The weight of the gold fixed on the interior should be determined by special weighings, so as to be able to find the value of it in water, simultaneously with that of the steel. The exterior surface of the bomb was also nickel-plated, to render it less oxidisable.

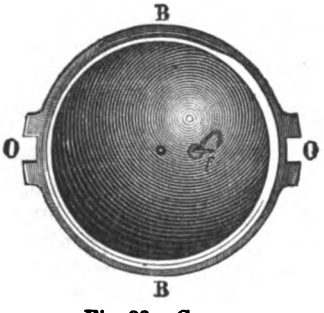

Fig. 22.—Cover.

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The cover carries laterally an insulating ivory fitting traversed by a platinum wire, *f f*, which is fitted with a small screwed portion, which holds it in the ivory. By this wire the electric spark is made to pass.

In every experiment, before closing the apparatus, a small mica disk, pierced in the centre, is fitted to the surface of the ivory to protect the latter from the flame of the explosion. The gases are introduced at the outset, and extracted at the end

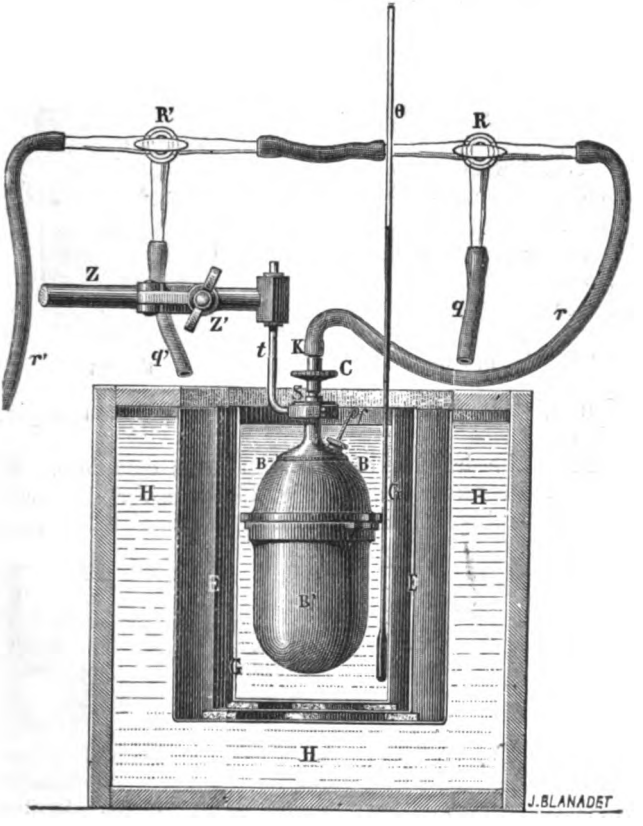

Fig. 23.—Bomb suspended in the calorimeter.

by the aid of a mercury pump, combined with an apparatus similar to Regnault's eudiometer, but greater in capacity (half a litre); this introduction being effected through an orifice, *p*, which can be stopped at will by the screw VV, fitted with a head C and a channel KK'.

Fig. 23 shows the calorimetric bomb in place inside the calorimeter, with its supports and the glass three-way cocks for operating it.

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6. M. Golaz also constructed for the author another apparatus of a similar form, wholly of platinum internally, covered externally with sheet steel. The screw and the tube which it traverses are entirely of platinum, which allows of passing chlorine, and sulphuretted or acid gases through it. The con-

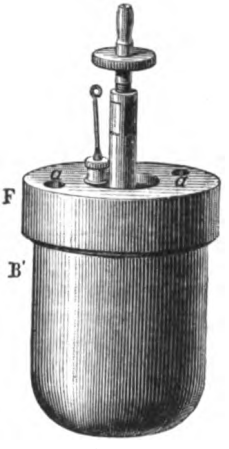

Fig. 24.

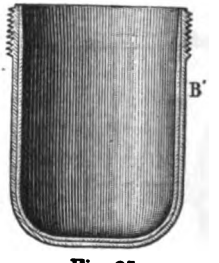

Fig. 25.

struction of this platinum screw is a real masterpiece of execution.

Fig. 24 is the drawing of this apparatus complete. Fig. 25 represents the receiver apart. Fig. 26, the cover fitted with the closing screw. Fig. 27, the tightening piece, F F, of the cover.

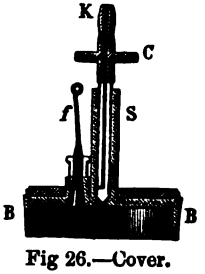

Fig 26.—Cover.

Fig 27.—Tightening piece.

Fig 28.—Auxiliary nut.

Lastly, Fig. 28, the auxiliary nut R, fitted with two pins *a*, *a'*, for screwing up the preceding piece. This nut does not form part of the apparatus immersed in the calorimeter.

The second apparatus has an internal capacity equal to 247 cms., contains 662 grms. of platinum and 419 grms. of steel, and is equivalent in water to 70·4 grms.

Its dimensions have been arranged so as to make it act in the calorimeter of 1 litre, containing only 550 grms. of water.

7. By proceeding in this way, the elevation of temperature may amount to 1·5° to 2·0°.

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The calorimetric measurements, carried out to within $\frac{1}{200}$ of a degree, involves a smaller error than by the old method, seeing that the combustions are generally total, and the corrections extremely reduced, through the short duration of the experiment.

However, the accuracy is limited by the weight of the substance on which we are obliged to operate; the weight of the carbonic acid formed generally not exceeding 0·200 grms. to 0·300 in the most favourable cases.

The quantity of gas burnt may be estimated either from its initial volume, or from the weight of its products.

The estimation of the initial volume presents great difficulties, owing to the necessity of taking into account the internal spaces of the tubes joining the bomb to the receivers in which the gases are measured. It has, however, been effected in the case of hydrogen.

But in the majority of cases it is preferable to weigh, after combustion, the gaseous products, which reduce themselves ordinarily to carbonic acid. With this object the gases are collected from the bomb, after explosion, by means of a mercury pump, and passed through a tube filled with pumice-stone and sulphuric acid, which dries them, then through a Liebig tube filled with potash, followed by a U tube filled with solid potash, in order to absorb the carbonic acid. The bomb is thrice filled with air free from carbonic acid, in order to clear out the gases completely, and each time the gases extracted from the bomb are passed through the Liebig tube. The latter, and the tube filled with solid potash, are finally weighed. It is necessary to further make the following verifications.

In the first place, the combustion of each gas is effected in the eudiometer, over mercury, in order to see that it is pure and gives the theoretical figures.

Then a similar combustion is carried out in the calorimetric bomb, the whole of the gases are extracted from it by the pump, and collected over mercury. After the absorption of the carbonic acid and of the oxygen, it is ascertained whether there remains any trace of combustible gas (carbonic oxide, hydrogen, marsh gas, etc.).

This verification is made, first with the aid of acid cuprous chloride, then by means of a fresh attempt at burning, by a proper quantity of oxygen. If nothing burn, there is added to the mixture the half of its volume of electrolytic gas, and the attempt is repeated.

In this manner it has been ascertained that the combustions are total with all hydrocarbon gases properly so called, such as methane, methene, ethylene, ethene, ethane, dimethyl, propylene, etc.

8. The combustion of nitrated, chlorinated, brominated, iodated

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and sulphuretted gases can likewise be effected in the platinum detonator which has just been described.

9. Not only are permanent gases burnt in the apparatus above described, but it is easy to burn in them every vapour the tension of which is sufficient for it to be completely transformed into gas in the volume of oxygen capable of completely burning it. In this case the liquid is weighed in a small sealed glass bulb, and the bulb is placed in the bomb; the latter is closed and filled with oxygen, then by a few shocks the bulb is broken. In a few moments after vaporisation has taken place the bomb is placed in the calorimeter. After five or six minutes, during which the thermometer is observed, the gas is exploded, and the carbonic acid is collected and weighed as above.

By proceeding in this manner we have the advantage of being able to control the weight of carbonic acid obtained, by the weight of the original liquid.

In the case of aldehyde, glycolic ether, hydrocyanic acid, hydrochloric and hydrobromic ethers, methylic and ethylic alcohols, etc., the operations have been carried out in the above way.

The combustions are total for every vapour having a considerable tension, such as that of bodies boiling below 50°.

But for the less volatile bodies, as benzene, there is no longer the same certainty of total combustion, probably owing to the condensation of some trace of matter on the walls and in the grooves of the apparatus. In this exceptional case, the detonation method loses some of its advantages and requires corrections similar to the ordinary method by combustion.

10. The figures obtained by detonation have not exactly the same significance as those obtained in the ordinary heats of combustion; the latter are carried out at constant pressure, the former at constant volume. By this method numbers are obtained which are better adapted to the majority of theoretical discussions.

It is, moreover, easy to pass from the numbers obtained at constant volume to those which would be obtained at constant pressure. According to the formula given above

$$Qtp = Qtv + 0{\cdot}5424\ (N - N') + 0{\cdot}002\ (N - N')t.$$

Take, for example, the combustion of carbonic oxide at 15°. $CO + O = CO_2$ liberates at constant volume + 68·0 Cal. In order to pass from this to the heat liberated at constant pressure we should note that on one hand CO occupies a unit of volume, O a half-unit. Therefore

$$N = 1\tfrac{1}{2}.$$

On the other hand CO_2 occupies a unit of volume.

$$N' = 1$$
$$N - N' = \tfrac{1}{2}.$$

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At 0° we should therefore have for the difference between the heats of combustion at constant pressure and at constant volume

$$+ 0{\cdot}54 \times \tfrac{1}{2} = + 0{\cdot}27.$$

At 15° to this figure must be added + 0·03, which raises the correction to + 0·30. The heat of combustion of carbonic oxide at constant pressure and at 15° will therefore be + 68·3 Cal.

Take again the combustion of ethane—

$$C_2H_6 + O_7 = 2CO_2 + 3H_2O$$
$$N = 1 + 3\tfrac{1}{2} = 4\tfrac{1}{2}$$
$$N' = 2 \text{ (assuming water liquid)}$$
$$N - N' = 2\tfrac{1}{2}.$$

The difference between the two heats of combustion is expressed at 15° by + 1·425 Cal.

The correction relative to condensation should in principle be reduced by a small quantity on account of the appreciable tension of water vapour at 15°, but this quantity may be neglected, owing to its smallness, in the present calculation.

11. We should, on the contrary, bear in mind that the correction due to the formation of water vapour is very appreciable in the calculation of the heat of combustion at constant volume, as well as at constant pressure, seeing that it represents the formation of gaseous water, which liberates less heat than the formation of liquid water. It has been verified in all these experiments from the internal capacity of the bomb, and conformably to Regnault's tables for the tension of water vapour and the vaporisation heat of water, at the temperature of the calorimeter.

12. More than three hundred explosions have been effected in these instruments. No accident has occurred in the instruments themselves, in spite of the magnitude of the sudden pressures developed during the explosions. These pressures are estimated at fifty atmospheres in certain cases where previously compressed gaseous mixtures have been operated upon.

13. We have, however, twice observed the spontaneous explosion of the gaseous mixtures while they were being shaken in closed and very dry glass vessels, with mercury. This very serious and singular accident appears due to internal electric sparks, produced by the friction of the mercury on the glass of the flasks, these being held in the hand and realising conditions of condensation similar to those of a Leyden jar.

14. We shall now expound the data of a determination, with the object of showing the method followed in the experiments, verifications and calculations.

Ethane.—The gas was prepared by the electrolysis of potassium acetate. It was freed from carbonic acid by potash, from ethylene by bromine, and from carbonic oxide by a pro-

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longed shaking over mercury with its own volume of acid cuprous chloride.

Its composition was verified; 102 vols. of this gas, burnt in the eudiometer by a slight excess of oxygen (360 vols.), produced 200·5 vols. of carbonic acid. The total diminution of the volume after explosion and absorption of carbonic acid, amounted to 451 vols.; the remainder, deprived of the excess of oxygen by hydrosulphite, yielded two volumes of nitrogen.

According to the formula $C_2H_6 + O_7 = 2CO_2 + 3H_2O$, 100 vols. of combustible hydrocarbon should have produced 200 vols. of carbonic acid, occasioning a total diminution of 450 vols.

The gas analysed was therefore ethane, containing only two hundredth parts of nitrogen, which have no appreciable influence on the heat of combustion.

The foregoing results show that the gas employed is really ethane, and that its combustion by a slight excess of oxygen is total. However, it has appeared useful to prove that the combustion is effected in the same manner in the calorimetric bomb, that is to say, that the above equation is applicable to the measurement itself.

With this object, the bomb was filled with the mixture of ethane and oxygen in suitable proportions, placed in the water of the calorimeter, and the gases exploded; then the whole of the gases contained in the bomb were extracted by the aid of a mercury pump, passed into a large test-tube, in which the carbonic acid was absorbed by potash and the excess of oxygen by hydrosulphite.

It is known that this reagent does not act either on carbonic oxide or on hydrocarbons. The residuum thus obtained underwent no diminution of volume by cuprous chloride, it was not combustible, and, mixed with half of its volume of oxygen, it did not explode under the influence of the electric spark. In another trial, for greater certainty, the analogous residuum was mixed with its own volume of electrolytic gas after adding oxygen to it, in order to burn the last traces of combustible gases, if such existed. But this test showed that there remained in the residuum nothing but nitrogen. The combustion of the ethane in the calorimetric bomb had therefore been total, as well as in the eudiometer.

The following are the figures of a calorimetric experiment performed on October 28, 1880.

200 cub. cms. of ethane and 720 cub. cms. of pure oxygen were mixed over mercury, and the mixture was passed, with the aid of a system of suitable tubes, into the calorimetric steel bomb lined with platinum, shown on p. 152, a vacuum having previously been created in the bomb with the aid of the mercury pump. The cock of the bomb was closed, and the latter was

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introduced into a platinum calorimeter of a capacity equal to 1 litre. Owing to the displacement produced by the bomb 550 cub. cms. of water sufficed to fill the calorimeter and cover the bomb, with the exception of the screw-cock. The thermometer, which served at the same time for stirrer, was put in place. The value in water of the calorimeter, the thermometer, and of the bomb amounted to 770·4 grms.

The whole was left at rest for some time, in order to allow the equilibrium of temperatures to become established. This accomplished, the following is the course of the thermometer:—

At the outset	13·295°
After 1 minute	13·295°
„ 2 minutes	13·295°
„ 3 „	13·295°
„ 4 „	13·295°
„ 5 „	13·295°

The explosion is then caused by passing a single spark, supplied by a very small induction coil and a bichromate cell. The noise of this explosion is faint, but appreciable with ethane; this gas, and diallyl, have produced the greatest noise. Often, in this kind of experiments, the noise of explosion is not even heard, and its existence only known by the heating of the water in the calorimeter.

The following is the continuation of this experiment:—

After 6 minutes (from the outset)	14·740°
„ 7 „	14·745°
„ 8 „	14·735°
„ 9 „	14·725°
„ 10 „	14·715°
„ 11 „	14·705°
„ 12 „	14·695°

The readings are suspended.

It will be noticed how short the combustion is, and how sharply defined are the phases of the calorimetric measurements. This done, the carbonic acid is extracted from the bomb with the aid of the mercury pump, it is dried by passing it through a curved tube of concentrated sulphuric acid, and a U tube filled with pumice-stone and sulphuric acid, then it is slowly passed through a Liebig tube with liquid potash, followed by a small U tube with solid potash.

The extraction being carried out, and the vacuum established down to a few millimetres of mercury, air (freed from carbonic acid) is allowed to enter the bomb, then this air is extracted by the pump and passed in its turn through the potash. This operation is thrice repeated in order to extract the last traces of carbonic acid formed by the combustion. The extraction lasts altogether about a quarter of an hour. When it is accomplished, the Liebig tube joined to the U tube is weighed, the increase of

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weight being equal to the weight of carbonic acid formed. It has been found to be 0·2090 grm. in the above experiment. This being established, let us calculate the heat produced. It is equal to the product of the masses reduced to water and multiplied by the variation of temperature; $\Sigma\mu + \Delta t$.

$$\Sigma\mu = 550 + 77{\cdot}4 = 627{\cdot}4,$$
$$\Delta t = 14{\cdot}745 - 13{\cdot}295, \text{ or } 1{\cdot}45° + \rho,$$

ρ being the heat lost by cooling.

Now, in the initial period of five minutes which preceded explosion there was neither gain nor loss. The maximum was established one minute and a half after explosion. In the five following minutes (final period) the loss was regular and equal to 0·01° per minute. This being determined between the fifth and the sixth minute the loss may be estimated at the half, or 0·005°; between the seventh and eighth it is 0·01°. The total correction will therefore be 0·015, which makes $t = 1{\cdot}465°$.

The heat liberated is $627{\cdot}4 \times 1{\cdot}465 = 919{\cdot}14$ cal. But this figure does not correspond to a total transformation of ethane into gaseous carbonic acid and liquid water. In fact, a certain quantity of water retains the gaseous state in the interior of the bomb. This quantity is easy to calculate, for it corresponds to the maximum tension of water vapour at 14·74°, viz. 12·5 mms. according to Regnault's tables. The capacity of the bomb being 247 cub. cms., and the density of water vapour at 14·7° being supposed theoretical (which is very near the reality, according to Regnault's experiments), the real weight of the gaseous water remaining in the bomb may be estimated at

$$0{\cdot}806 \text{ grm.} \times \frac{247}{1000} \times \frac{12{\cdot}5}{760} \times \frac{1}{1 + 0{\cdot}00367 \times 14{\cdot}74} = 0{\cdot}0031 \text{ grm.}$$

Now, the vaporisation of this weight of water at 15°, still following Regnault, absorbs $-1{\cdot}85$ cal., a quantity which must be added with the contrary sign to 919·14 cal., which makes in all + 920·99 cal. This is the heat liberated by the combustion of the weight of ethane which gave 0·2090 grm. of carbonic acid.

But 1 equiv. of ethane $C_2H_6 = 30$ grms., would have yielded 88 grms. of carbonic acid. It is therefore sufficient to calculate the heat liberated by the formation of 88 grms. of carbonic acid to obtain the heat of combustion of ethane at constant volume, viz. 387·78 Cal.

At constant pressure this figure must be increased by 1·425, according to the formula on page 154, which makes 389·21 Cal. This is the heat of combustion of ethane deduced from the above experiment.

15. The method just described has been applied to the study

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of the combustion of the following thirty gases and vapours, all *combustible bodies*.[1]

Hydrogen.

Carbonic oxide.

Hydrocarbons, such as methane, ethane, ethylene, acetylene, hydride of propylene, propylene, allylene, benzine, dipropargyl, diallyl.

Oxygenated compounds, such as methylic ether, glycolic ether, aldehyde, methylformic and ethylformic ethers, dimethylic methylal.

Nitrated compounds, such as cyanogen, hydrocyanic acid, trimethylamine, ethylamine.

Chlorated, bromated, iodated compounds, such as methylchlorhydric, methylbromhydric, methyliodhydric, ethylchlorhydric and ethylbromhydric ethers, chlorides of methylene and ethylidene.

Sulphuretted compounds, such as carbon disulphide.

It has also been used by an inverse process to measure the heat of formation of the combustive gases, such as nitrogen monoxide, and nitric oxide (p. 149), the heat of formation of these gases being deduced from the difference between the heats of combustion of the same carburetted (*carboné*) gas by pure oxygen on the one hand, and by the oxygenated gas on the other.

[1] "Annales de Chimie et de Physique," 5e série, tom. xxiii. p. 115 and following.

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CHAPTER III.

HEAT OF FORMATION OF THE OXYGENATED COMPOUNDS OF NITROGEN.

§ 1. Preliminaries.

1. Potassium nitrate, otherwise termed nitre, or saltpetre, has been employed for many centuries as an ingredient of gunpowder. Its use was discovered by empirical means; but theory only commenced to throw a light upon it a century ago, when the part played by oxygen in combustion was discovered by Lavoisier, as well as the presence of a great quantity of oxygen in potassium nitrate, but the difference between these two substances as regards their explosive action has only become clear within the last few years, as being due not to a difference in chemical composition, but rather as explicable on thermochemical grounds.[1]

The determinations in question presented extraordinary difficulties, and the results were not realized at the first attempt. They only reached their full accuracy after a series of experiments.

Attention has since been directed towards obtaining more exact values, and the scope of the work has been extended to the heat of formation of the various oxygenated compounds of nitrogen, and its theoretical importance has therefore considerably increased. The following are the results obtained with nitric oxide, which is the origin of most of the others.

§ 2. Heat of Formation of Nitric Oxide.

1. The series of the five oxides of nitrogen, formed in proportions varying according to simple ratios of weight and volume,

[1] The measurement of the heat of formation of potassium nitrate involved an elaborate series of experiments, based partly on the previous determinations of Dulong, Hess, Graham, Favre and Silbermann, Andrews, Wood, Thomsen, Deville and Hautefeuille, Bunsen and Schischkoff, etc., but largely on experiments begun in 1870 by the author; and the following data, relating to the heat of formation of the oxygen compounds of nitrogen, were an outcome of this investigation.—Eds.

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is one of the most important in chemistry. The knowledge of the heats of formation of these oxides offers the more interest as the two first are formed with absorption of heat from their elements, while the three others are, on the contrary, formed with liberation of heat from nitric oxide, which plays the part of a true radical. A knowledge of the heats of formation of these bodies is, moreover, indispensable to the theoretical study of explosive substances, of which they go to form the greater part. Unfortunately, the exact determination of these quantities presents great difficulties, as is the case with combinations which cannot be brought about by direct synthesis.

The figure deduced by Favre and Thomsen, namely 26·7 Cal., from the action of chlorine on ammonia, was found to be wide of the truth by the author, who estimated it at 12·2 Cal., and this last figure has since been confirmed by Thomsen, so that all values up to that date in which the formation of ammonia intervenes have to be corrected by 14·5 Cal. But, before applying such a correction to the heat of formation of the oxides of nitrogen, the author endeavoured, with success, to measure this more directly by comparing the heat of combustion of methene and of cyanogen when burnt in oxygen and in nitric oxide respectively. The results obtained were practically identical, and the method admits of rapid and exact manipulation, and the figures obtained are therefore incomparably more valuable than the previous ones based on no less than nine experimental data. The following are the details of the experiment.

The combustible chosen was cyanogen or ethylene. It was found that the slow combustion of a mixture of cyanogen, ethylene or carbon disulphide with nitric oxide always produced an abundance of nitrous vapours; but this is avoided by detonating the cyanogen and nitric oxide in the calorimetric bomb.

1. *Combustion of Cyanogen by free Oxygen.*

The explosion of the following gaseous mixture: 26 grm. $CN + O_2 = CO_2 + N$ liberated + 131·0, and + 130·7, the mean being: + 130·9; explosion at constant volume.

Hence we obtain the heat absorbed in the union of carbon (diamond) and nitrogen.

$$C \text{ (diamond)} + N = CN \text{ absorbs } - 36{\cdot}9.$$

In another series of experiments made by burning a jet of cyanogen in oxygen at constant pressure + 131·6, for the heat of combustion, and − 37·6, for the heat of formation, were the figures obtained. The numbers found, whether at constant pressure or at constant volume, can therefore be regarded as identical, which one would expect, as the combustion of cyanogen by free oxygen does not give rise to any change of

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volume. This remark applies likewise to the combustion of cyanogen by nitric oxide.

2. Combustion of Cyanogen by Nitric Oxide.

The explosion of the following gaseous mixture, $CN + 2NO = CO_2 + N_2$ gave + 175·3; + 172·9; + 175·0; + 174·4; + 175·3; the mean being 174·6; explosion at constant volume.

The difference between this number and the figure + 130·9 obtained with free oxygen under the same conditions, viz. the value + 43·7, represents the heat liberated by the decomposition of 2NO into its elements. According to these two data, the union of nitrogen with oxygen to form nitric oxide (NO 30 grms.), $N + O = NO$ absorbs − 21·8 Cal.

3. Combustion of Ethylene by free Oxygen and Nitric Oxide.

Similar experiments were made with ethylene, and yielded the same results. It is, therefore, unnecessary to enter into details. It will be sufficient to state that the difference between the numbers observed corresponding to the union of the elements nitrogen and oxygen $N + O = NO$, was − 21·6 Cal.

§ 3. Heat of Formation of Nitrogen Monoxide.

The heat of formation of nitrogen monoxide was measured by exploding carbonic oxide mixed first with this gas and then with oxygen and taking the difference of the two results.

1. Combustion of Carbonic Oxide by Oxygen.

CO (14 grms.) $+ O = CO_2$, liberated + 33·7 and + 34·4. The mean, + 34·0, refers to the explosion at constant volume.

From this we pass to the heat of the combustion at constant pressure [1] by adding 0·14, by reason of the condensation which reduces $1\frac{1}{2}$ vols. of the explosive mixture to 1 vol.; we thus obtain 34·14 cals. This figure agrees almost exactly with that previously obtained by the combustion of a jet of carbonic oxide in oxygen, viz. + 34·09.[2] It also agrees with the value obtained by the wet process [3] with formic acid, by oxidizing on one hand the formic acid, and on the other hand transforming it into water and carbonic oxide. By this method the combustion of carbonic oxide gave + 34·25.

2. Combustion of Carbonic Oxide by Nitrogen Monoxide.

$CO + N_2O$, 22 grms. $= CO_2 + N_2$ liberated; + 44·0; + 45·1; + 44·1, the mean being 44·4; explosion at constant volume.

[1] "Essai de Mécanique Chimique," tom. i. p. 115.
[2] "Annales de Chimie et de Physique," 5e série, tom. xiii. p. 13.
[3] Same collection, tom. v. p. 316.

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According to theory this number is the same at constant pressure.

It follows from these figures that the formation of nitrogen monoxide from nitrogen and free oxygen at constant pressure $N_2 + O = N_2O$ absorbs + 34·1 − 44·4 = − 10·3; or for $N_2 + O = N_2O$ 44 grms. − 20·6 Cal.

The heat absorbed in the formation of the monoxide (− 10·3) is practically one half of the heat absorbed in the formation of nitric oxide (− 21·6).

§ 4. Heat of Formation of Dissolved and Anhydrous Nitrogen Trioxide, and the Nitrites.

1. The heat of formation of nitric oxide being known, it is easy to obtain from it those of the higher oxides; for it is easy to change nitric oxide, under conditions of calorimetric experiments, into nitrogen pentoxide, tetroxide, and trioxide.

2. Conversion of nitric oxide into nitric acid by several methods. One method consists in first forming a nitrite and afterwards oxidizing it. In regard to the formation of nitrites, nitric oxide and oxygen react very rapidly upon each other, upon contact with an alkaline base, and are changed almost exclusively into nitrites whatever be the relative proportions of the two gases.[1]

This experiment was made in a closed vessel (Fig. 29) of a capacity equal to 800 cub. cms. almost filled with baryta water, the strength and weight of which was accurately measured.

This vessel served as a calorimeter; it was surrounded by an envelope, as in the annexed figure.

A calorimetric thermometer, θ, was plunged into the vessel, passing through a large tube, K, at the upper orifice of which it was fixed by a small cork, *b*. The vessel itself was closed by a large cork, pierced with four holes, one for the passage of the tube, K, another for that of a tube, *t*, conducting the nitric oxide and dipping into the liquid, a third hole (hidden by the large tube in the figure) received another tube for supplying the oxygen, lastly a tube, *s*, for carrying away the excess of the gases.

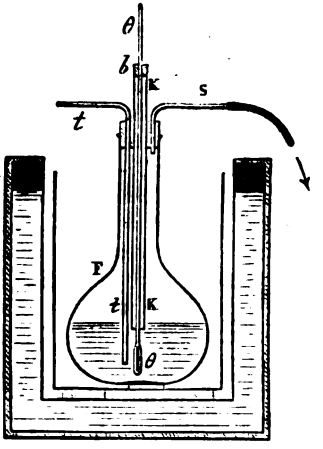

Fig. 29.

Having introduced separately into the calorimetric apparatus

[1] "Annales de Chimie et de Physique," 5e série, tom. vi. p. 193.

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dry nitric oxide and oxygen, and shaken them incessantly, the heat liberated and the increase of weight was measured and the amount of trioxide and pentoxide formed was ascertained. The weight of pentoxide formed is always very slight, it has been taken account of in the calculations according to the data on the following pages.

The following was found upon full calculation,

$$2NO + O + BaO = (NO_2)_2Ba, \text{ dissolved: } + 28{\cdot}0 \text{ Cal.}$$

3. *Barium Nitrite.*—In order to pass from barium nitrite in solution to nitrous acid, it was necessary to make a special study of barium nitrite itself, this salt being a perfectly pure and well-defined body, and intended to serve as starting point for other experiments on the respective transformation of the nitrous acid and of the nitrites into nitric acid and nitrates.

The barium nitrite was prepared by the reaction of nitrous vapour (starch attacked by nitric acid) on a mixture of barium carbonate and hydrate held in suspension in water. The barium nitrite obtained was several times recrystallized, and its purity verified by analysis.

This salt crystallizes in brilliant needle-shaped prisms, gathered together without order. Very slow spontaneous evaporation yields large, confused twin crystals, which have the appearance of a rather acute, double hexagonal pyramid. This is in reality a limiting form, belonging to the system of the straight rhomboidal prism, and analogous to that of potassium sulphate. The following are some thermal data relative to this salt:—

One equivalent $(NO_2)_2BaH_2O$, 123·5 grms. dissolved in 60 times its weight of water absorbs at 12°, − 4·3 Cal.

The dissolving of the anhydrous salt $(NO_2)_2Ba$ = 114·5 grms. absorbs at 12°, − 2·84 Cal.

It follows from these figures that the reaction $(NO_2)_2Ba$ solid + H_2O liquid = $(NO_2)_2BaH_2O$ solid, liberates + 1·46.

The very weak solution of barium nitrite, decomposed by dilute sulphuric acid, liberates for 1 equivalent, + 7·9 Cal.

Very dilute nitrous acid is set free under these conditions without very sensible formation of nitric acid, as is proved by adding potassium permanganate to it. Further, the formation of barium sulphate, according to experiments made under the same conditions of dilution and temperature, liberates + 18·50; starting from sulphuric acid and the diluted base.

From these figures we may conclude that, N_2O_3 very diluted + BaO diluted = $Ba(NO_2)_2$ diluted, liberates + 10·6. This is 3·2 Cal. less than nitric and hydrochloric acid, which shows that nitrous acid must be ranked among the weak acids.

Dilute hydrochloric acid completely displaces nitrous acid

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from alkaline nitrites, according to the thermal measurements, while in presence of baryta, dilute acetic acid, weaker than hydrochloric acid, gives rise to a division, variable according to the relative propositions.

This division may be explained by partial dehydration, that is to say, by the state of partial dissociation of the hydrate of nitrous acid in its solution.

4. *Ammonium nitrite.*—This salt in the solid form has been but little studied. The author having had occasion to prepare it for thermo-chemical researches, several new facts have been observed. It was prepared by decomposing pure barium nitrite by ammonium sulphate in exactly equivalent proportions in the cold. The filtered liquid was evaporated in vacuo over caustic lime, at ordinary temperatures. The operation lasted several weeks, and, owing to decomposition, even then the yield was only thirty to forty per cent. of that required by theory. It is necessary to evaporate, to complete dryness, and to preserve the solid salt in vacuo, over caustic lime. The mass is white, crystalline, somewhat elastic and tenacious, so that it may be moulded between the fingers, and adheres to the sides of the containing vessel. It is perfectly neutral, and corresponds to the formula $(NH_4)\,NO_2$. It is very diliquescent. At the ordinary winter temperature, it decomposes very slowly; at that of summer more rapidly. Heated to 60° or 70° on the water bath, it detonates violently after a few seconds. It detonates also by a blow from a hammer. Its decomposition disengages weight for weight about three quarters as much heat as nitroglycerin, hence its activity. It cannot be kept in sealed tubes, because they soon explode, from the pressure of the gases generated. It is best kept as above.

If the decomposition take place with explosion, it yields only nitrogen. When gradually decomposed by progressive heating, the salt loses at first a little ammonia, and afterwards yields, together with free nitrogen, a small amount of the monoxide, nitric oxide, and trioxide vapour.

Its very slow decomposition, at the ordinary temperature, yields nitrogen and water, without affecting its neutrality.

Aqueous concentrated solutions decompose more rapidly than the dried salt in the cold, so that when agitated, they evolve gas like champagne. Ammonium nitrite may be formed synthetically by mixing together nitric oxide, ammonia, and oxygen. The solid nitrite condenses on the walls of the tube in crystalline masses, apparently cubical in form.

The three gases immediately react on each other, but as they do not contain the water necessary for the constitution of ammonium nitrite, nitrogen is formed at the same moment.

$$2NO + O + 2NH_3 = 2N_2 + 3H_2O.$$

$$2NO + O + 2NH_3 + H_2O = 2NH_4NO_2.$$

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Both reactions, in fact, are simultaneously developed, but the volume of the nitrogen collected is much greater than that which should be produced if the whole of the available water were changed into ammonium nitrite. In the above experiments it represented more than double the theoretical quantity, which is easily explained by the simultaneous decomposition of a portion of the nitrite. An analysis showed that the products did not contain any sensible proportion of nitrate.

The following are various thermal data relative to ammonium nitrite. NH_4NO_2 (64 grms.) dry + 120 times its weight of water at 12·5° absorbs in dissolving 4·75 Cal. The heat liberated when dilute nitrous acid unites with ammonia may be deduced from the heat liberated when ammonium sulphate is precipitated by barium nitrite, N_2O_3 dilute + NH_3 dilute + H_2O liberates + 9·1.

The heat liberated by its decomposition into nitrogen and water, NH_4NO_2 solid = N_2 + $2H_2O$ liquid, amounts, according to the formula, to + 73·2; the water being gaseous, we should have + 54 Cal.

5. *Silver nitrite.*—By double decomposition with solutions of different degrees of concentration N_2O_3 dissolved, + Ag_2O precipitated = $2AgNO_2$ dissolved, liberates + 3·36. N_2O_3 dissolved, + Ag_2O precipitated = $2AgNO_2$ crystallised, liberates + 12·1.

The heat absorbed in the solution of an equivalent of silver nitrite is equal to − 8·74 Cal.

It is worthy of remark that the thermal formation of solid silver nitrite + 82·1 exceeds that of silver nitrate + 10·9, both formations being reckoned from the diluted base and acids: while the formation of the alkaline nitrates, such as solid barium nitrate, liberates + 18·6, and that of ammonium nitrate calculated from the same components + 18·7, figures which are on the contrary higher than the heat of formation of the corresponding nitrites. In fact, the formation of solid barium nitrite liberates only + 13·4, and that of solid ammonium nitrite + 13·8.

These relations deserve some attention, for they tend to connect the nitrites with the chlorides and halogen salts, in the case of which the thermal formation of the salts of silver, calculated in a similar manner, exceeds even that of the alkaline salts. Such relations are in conformity with the known analogies between the group (NO_2) which plays the part of a radical compound in the nitrites, and the simple radical halogens, such as chlorine and its congeners; in other words, $Ba(NO_2)_2$ is here compared to $BaCl_2$ and $AgNO_2$ to AgCl.

6. *Formation of nitrogen trioxide.*—The preceding numbers concerning barium nitrite being known, the heat liberated by the transformation of nitric oxide into dilute nitrous acid, is

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deduced from them, thus: $2NO + O +$ water $= N_2O_3$ dilute $+ 28{\cdot}0 - 10{\cdot}6 = 17{\cdot}4$ Cal.[1]

From this figure, and from the heat of formation of nitric oxide, is deduced the formation of dilute nitrogen trioxide from its elements, nitrogen and oxygen. $N_2 + O_3 +$ water $= N_2O_3$ dilute, absorbs $- 4{\cdot}2$ Cal.

The experiments relative to the formation of nitrogen trioxide might be quoted here, but these experiments will be more conveniently described after those relating to nitric peroxide. The numerical result will suffice at present:—

$\frac{1}{2}(N_2 + O_3) = \frac{1}{2}(N_2O_3)$ gas absorbs $- 11{\cdot}1$ Cal., or for N_2O_3 $- 22{\cdot}2$ Cal.

7. *Formation of the nitrites from their elements.*—According to the above numbers, the thermal formation of the nitrites from their elements liberates—

	Salt dissolved.	Salt anhydrous.
Potassium nitrite, $N + O_2 + K = KNO_2$ ...	$+ 88{\cdot}7$ ...	—
Sodium nitrite, $N + O_2 + Na = NaNO_2$ ...	$+ 84{\cdot}0$ ...	—
Ammonium nitrite, $N_2 + O_2 + H_4 = NH_4NO_2$	$+ 60{\cdot}0$ ...	$+ 64{\cdot}8$
Barium nitrite,[2] $N_2 + O_3 + BaO = Ba(NO_2)_2$	$+ 26{\cdot}8$ ...	$+ 29{\cdot}6$
Silver nitrite, $N_2 + O_2 + Ag = AgNO_2$ ...	$+ 2{\cdot}7$ ...	$+ 11{\cdot}4$

§ 5. Heat of Formation of Nitric Peroxide.

1. The heat of formation of this body was measured by two inverse methods, and according to three distinct processes, intended to control one another, viz.

(1) By synthesis or by the direct reaction of nitric oxide on oxygen, both gases being employed in equivalent ratios.

(2) By the transformation of the already formed nitrogen tetroxide into nitric acid by means of chlorine and water. By the transformation of the same nitric peroxide into barium nitrate by means of barium dioxide, whence we pass by calculation to the transformation effected by means of free oxygen. The heat liberated by the direct metamorphosis of nitric oxide and oxygen into dilute nitric acid, being known from former

[1] Favre had estimated this quantity at $-6{\cdot}6$ Cal. from erroneous data. Thomsen calculated $+ 18{\cdot}2$, relying upon the union of three more exact thermal data, one derived from the reaction of nitric oxide, and oxygen forming nitric peroxide ($+ 19{\cdot}57$), another from the dissolving of the latter body in water ($+ 7{\cdot}75$), a solution which he supposes to give rise to nitric acid and nitrous acid in equal equivalents, the last datum being deduced from the reaction of chlorine on the same solution, which it changes entirely into nitric acid. This method is much more complicated than the one applied above, and is founded on less sure reactions. However, the results coincide sufficiently.

[2] The heat of formation of this salt has been given from baryta only, the heat of oxidation of barium being unknown. In the transformation of barium nitrite as well as in that of the nitrate, this datum moreover suffices for all calculations relative to explosive substances, as these calculations can always be established from the baryta itself.

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experiments, we deduce from the latter trials by difference the heat which would be liberated by the metamorphosis of nitric oxide and of oxygen into nitric peroxide.

The first method, though simpler, is less exact than the others from a consideration of the weight of the gases employed, and of the quantity of heat produced.

2. *First process. Nitric oxide and oxygen.*—Two concentric glass bulbs are enclosed one inside the other and sealed separately, each containing one of the dry gases in the exact ratio of 2 volumes nitric oxide (250 to 280 cub. cms.) to 1 volume of oxygen (see Fig. 30).

The system is plunged into the water of the calorimeter, then by a jerk of the hand the internal bulb is broken, leaving its envelope intact. Both gases react at once, and the action is allowed to complete itself. The nitric peroxide remains gaseous even up to 10° or 15°, because its tension in the bulb is less by a third than the atmospheric pressure. The latter circumstance slightly lowers the figures which would be observed at the normal pressure, viz. by 0·3 Cal. (p. 155).

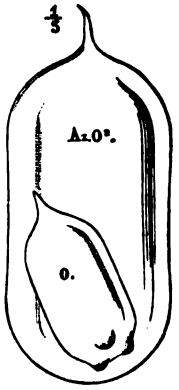

Fig. 30.

Operating in this way and calculating the reaction at constant pressure[1] the following was observed:—$2NO + O_2 = N_2O_4$ gas + 19·6; + 19·9 + 18·3 + 19·8 : mean + 19·4 Cal.

3. *Second process. Nitric peroxide, gaseous chlorine and water.*—In principle, this reaction is the following:—NO_2 gas + Cl gas + H_2O + water = HNO_3 dilute + HCl dilute.

The heat of formation of water (34·5 for $H_2 + O$) and that of dilute hydrochloric acid + 39·3 for H + Cl + water = dilute HCl being taken as known.

In practice it has been found preferable to operate on liquid nitric peroxide, and this led the author to determine its heat of vaporisation,[2] viz. 4·33 Cal. for $NO_2 = 46$ grms.

The weighing of liquid nitric peroxide may be performed very accurately in a hermetically sealed bulb.

In order to weigh chlorine directly in the same way, recourse was had to the following artifice. Instead of allowing the nitric peroxide and the chlorine to act directly on the water, the chlorine was absorbed by a dilute solution of potash, the latter being in excess, the heat liberated and the weight of chlorine absorbed was determined by means of the vessel shown on page 163.

[1] Thomsen obtained + 19·57 by introducing both gases simultaneously into a chamber placed in a calorimeter.

[2] See the method employed ("Annales de Chimie et de Physique," 5e série, tom. v. p. 154).

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A volume of the alkaline solution containing a weight of chlorine precisely equal to that of the nitric peroxide was then taken, and the bulb containing the acid placed in it. The bulb was then opened by the breakage of one of its points, taking care that the mixture of the two solutions should be gradual, and the heat liberated during the reaction measured.

Lastly, an excess of dilute hydrochloric acid is added to the solution, the heat liberated by this addition being also measured. Thus the whole is brought to a very simple final state, that of a weak aqueous solution, formed by an equivalent of potash, an equivalent of nitric acid, and a known proportion of hydrochloric acid somewhat greater than an equivalent.

In an independent experiment the heat liberated by the mixture of the three components taken directly in the same proportions and degree of dilution as in the above experiment was measured.

This being known it is easy to deduce from the data obtained the heat liberated by the following transformation :—

NO_2 gas + Cl gas + H_2O + water = HNO_3 dilute + HCl dilute.

The weight of NO_2 being 2·281 grms.	... ...	17·9 Cal.
„ „ „ 1·125 grms.	... ...	17·7 „
Mean	... ...	17·8 „

deducting from this value the difference in the heats of formation of dilute hydrochloric acid, viz. :—

$$39{\cdot}3 - 34{\cdot}5 = + 4{\cdot}8,$$

we find, $2NO_2$ liquid + O gas + water = $2HNO_3$ dilute + 13·0. Adding now the heat of vaporisation of nitric peroxide, we obtain $2NO_2$ + O gas + water = $2HNO_3$ dilute + 17·3.[1]

The heat liberated by the transformation of nitric oxide and oxgyen into dilute nitric acid, + 35·9 Cal., being taken as known, we shall definitely have for the heat liberated by the formation of gaseous nitric peroxide, from its immediate components, $2NO + O_2 = 2NO_2$ gas + 35·9 − 17·3 = 18·6 according to the experiments of the second process.

4. *Third Process. Nitric peroxide and barium dioxide.*—This process is based on the following reactions, $2NO_2 + BaO_2 = (NO_3)_2Ba$. But this reaction does not take place with pure and anhydrous bodies under the conditions adapted for calorimetric measurements, and the following method was used.

The liquid nitric peroxide is weighed in a bulb, then the

[1] Thomsen obtained for this reaction the value + 16·9. In order to measure it, he adopted the following process, which is less certain than that indicated in the test. He allowed the nitric peroxide gas to act upon water, so as to dissolve it, which liberates + 7·75; then he introduced chlorine into the liquor, which liberates + 14·28 more, and he derives from these data the heat of oxidation of nitric peroxide gas, forming dilute nitric acid.

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equivalent barium dioxide is weighed, the latter is dissolved in dilute hydrochloric acid and the heat liberated measured. Next, nitric peroxide is allowed to react gradually upon the solution which escapes from one of the broken points of the bulb which is completely immersed in the solution. The heat liberated during this second reaction is also measured.

The sum of the two results gives the total heat corresponding to the following transformation—

$2NO_2$ liquid + BaO_2 anhydrous + 2HCl dissolved = $2HNO_3$ dissolved + $BaCl_2$ dissolved.

It is immaterial whether we suppose the baryta united with the hydrochloric acid, or with the nitric acid, or shared between both, since the heat liberated by the union of this base with either acid is the same.

The foregoing experiment was made with pure and anhydrous barium dioxide.

The heat of formation from anhydrous baryta and free oxygen—

$$BaO + O = BaO_2 \text{ liberates } + 6{\cdot}05 \text{ Cal.}^1$$

This quantity being known, as well as the heat of solution of anhydrous baryta in dilute hydrochloric acid (+ 27·8); lastly, the heat liberated by the reaction of nitric acid (formed from nitric peroxide) upon dilute barium chloride being sensibly *nil*; the calculation of the experiments made with nitric peroxide enables the heat liberated in the following reaction to be arrived at—

$$2NO_2 \text{ liquid} + O \text{ gas} + H_2O = 2HNO_3 \text{ dilute.}$$

Thus—

	Weight.	Found.
NO_2	2·279	+ 12·4 Cal.
NO_2	1·358	+ 12·2 „
NO_2	0·951	+ 12·6 „
	Mean	+ 12·4 „

In order to pass to gaseous NO_2 we must add the heat of vaporisation of this body, viz. + 4·33; which makes altogether + 16·73.

Finally, this number deducted from the heat of formation of dilute nitric acid by nitric oxide and oxygen (viz. + 35·9) gives for the formation of nitric peroxide gas from nitric oxide and oxygen, + 35·9 − 16·73 = + 19·17.

5. To sum up, the reaction NO + O = NO_2 gas liberates—

According to direct experiment	+ 19·4
„ „ the reaction of nitric peroxide gas on chlorine ...	+ 18·57
„ „ the reaction of nitric peroxide on barium dioxide	+ 19·17
Mean	+ 19·04

[1] "Annales de Chimie et de Physique," 5e série, tom. vi. p. 209.

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The heat of formation of nitric oxide itself from the elements being − 21·6, from it is deduced that of nitric peroxide gas. $N + O_2 = NO_2$ gas, absorbs − 2·6. The formation of liquid nitric peroxide on the contrary liberates heat, viz. + 1·7.

6. The figures which express the heat of formation of nitric peroxide gas, whether from nitrogen and oxygen or from nitric oxide and oxygen, were obtained near the ordinary temperature. Their value, however, becomes notably altered when referred to a higher temperature. In fact, the specific heat of nitric peroxide gas varies very considerably with the temperature.[1] This gas undergoes, especially between 26° and 150°, a kind of molecular transformation of an exceptional order, which nearly doubles its density, in order to bring it to a value corresponding to the molecular weight $NO_2 = 46$ grms. This transformation may be estimated by supposing the theoretical specific heat of the gas constant and equal to the sum of those of its components.

We have thus found that the transformation absorbs

From	27 to 67°	2·65 Cal.
„	67 to 103°	1·75 „
„	103 to 150°	0·85 „
„	150 to 200°	0·03 „
	Total	5·28 „

This number, added to the heat of vaporisation properly so called, viz. 4·3, brings the heat absorbed to nearly 9·6. Hence it follows that the reaction of nitric oxide on oxygen, $NO + O = NO_2$ gas, liberates quantities of heat decreasing with temperature, at least from 26° up to about 200°. It produces only + 13·7 Cal. towards 200°. Similarly the formation of the compound from the elements,

$$N + O_2 = NO_2,$$

absorbs quantities of heat continually increasing in absolute value, or — 7·9 towards 200°.

These figures hardly vary from 200° to 250°. Beyond this they seem to decrease again, though much less rapidly, and in conformity with what happens in the case of carbonic acid and gases formed with condensation.[2]

7. *Formation of nitrogen trioxide.*—The calculation of the heat of formation of this acid has not been given above, because it is inseparably connected with the experiments relative to nitric peroxide. Take now the reaction

$$2NO + O = N_2O_3.$$

If this reaction could take place separately, it would suffice to bring together four volumes of nitric oxide and one volume of oxygen, and to measure the heat liberated.

[1] "Bulletin de la Société Chimique," 2e série, tom. xxxvii. p. 434. 1882.
[2] "Essai de Mécanique Chimique," tom. i. p. 334.

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But under these conditions a portion of the two gases is always changed into nitric peroxide, and it does not seem possible to obtain nitrogen trioxide without having at the same time the products of its transformation, NO_2 and NO, the whole constituting a system in equilibrium.

However, by increasing the proportion of nitric oxide, that of the nitrogen trioxide is increased. But we are limited in this respect by the necessity of operating upon a volume of oxygen sufficient to give notable calorimetric effects.

By carrying out the reaction by the aid of a system of concentric bulbs (see p. 168), containing a known volume of the two dry gases (about 400 cub. cms. of NO), the heat liberated was measured, the proportion of NO and NO_2 formed was determined by absorbing the products in a weak alkaline solution, the weight of oxygen employed affording a verifying equation.

The products being known as well as the heat of formation of NO_2, we can calculate the heat of formation of the nitrogen trioxide. The datum which results from these measurements, though less accurate than that of the other oxides of nitrogen, is nevertheless useful.

From the mean of three experiments, $2NO + O = N_2O_3$ gas liberates + 10·5 Cal. Hence the fixation of a second equivalent of oxygen, that is, the transformation of the nitrogen trioxide into nitric peroxide in the gaseous state, viz. $N_2O_3 + O = 2NO_2$ gas liberates + 19·0 − 10·5 = 8·5.

8. The fixation of a third equivalent of oxygen, transforming the peroxide into nitric anhydride. $2NO_2 + O = N_2O_5$ gas liberates + 2·0.

The heat liberated by the same weight of oxygen, at the ordinary temperature, decreases according as the oxygen increases in the compound of nitrogen, starting with nitric oxide, a fact which is demonstrated by the series of numbers + 10·5 + 8·5 + 2·0.

The latter figure is in keeping with the slight stability of nitric anhydride, a compound which cannot be formed from nitric oxide by direct synthesis.

9. Direct measurements, independent of all analysis, show that the same volume of oxygen, in the presence of an equal or more than double volume of nitric oxide, in sealed bulbs, liberates the more heat the greater the volume of nitric oxide, and consequently that of the nitrogen trioxide formed. This result contributes with the preceding ones to prove that the heat liberated in the formation of nitric peroxide gas is not double that liberated by the nitrogen trioxide gas, contrary to the relation existing between the weights of oxygen successively fixed.

Finally the formation of a nitrous gas from its elements at the ordinary temperature, calculated from the above data—

$$N_2 + O_3 = N_2O_3 \text{ gas, absorbs } - 22·2.$$

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§ 6.—Heat of Formation of Dilute Nitric Acid, of Monohydrated Nitric Acid and of Anhydrous Nitric Acid.

1. The heat of formation of nitric acid from its elements is a datum of the first importance, and may be deduced from that of nitric oxide. Several methods were employed. We shall first indicate them in principle and then give them in detail.

(1) By the Nitrites. Having first formed a nitrite in presence of a base, such as baryta, the barium nitrite is transformed into nitrate; and this by four distinct processes.

(2) By Nitric Acid and Barium Dioxide. The nitric oxide is dissolved in concentrated nitric acid, which changes it into nitrogen trioxide, the latter being further oxidised after dilution by barium dioxide.

(3) By Nitric Peroxide. This body is further oxidised by various agents, which have already been indicated. They may be employed either to measure the heat of formation of nitric peroxide, deduced from that of nitric acid, which is known, or to measure the heat of formation of nitric acid, that of nitric peroxide being known.

2. First method. Transformation of barium nitrite into nitrate. In this reaction barium nitrite is oxidised, and the heat liberated is measured by four processes distinct and independent of one another.

First process. Gaseous chlorine.—Initial system: $Ba(NO_2)_2$ dissolved; Cl_4 gas; H_4 gas; O_2 gas; nBaO dissolved; nHCl dissolved, these bodies being all separate from one another. Final system: $Ba(NO_3)_2$ dissolved; $4HCl$ dissolved; $n(BaCl_2 + H_2O)$ dissolved, these bodies being mixed.

It is first of all supposed that H_2 is allowed to react on O, which forms water, liberating + 69 Cal.; then the following experiments are carefully carried out. Dry chlorine is agitated with baryta water, of known strength and weight, in a calorimetric flask (p. 163); the heat liberated, Q, is measured, and the chlorine absorbed, p, is directly weighed to within 0·001 grm. Care is taken that there shall remain a considerable excess of free baryta, and agitation is kept up incessantly during the operation, in order to prevent the formation of any other oxide of chlorine than hypochlorous acid; the measurement of the heat liberated supplies a verification in this respect.[1]

A quantity of barium nitrite strictly equivalent to the weight of chlorine absorbed ($Ba(NO_2)_2$ for Cl_2) is then taken and dissolved separately in water, the solution is then mixed with that of the hypochlorite, an operation which liberates a quantity of heat, q, which can almost be neglected.

[1] "Annales de Chimie et de Physique," 5e série, tom. v. pp. 335–338.

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Dilute hydrochloric acid is at once added in considerable excess, which liberates a fresh quantity of heat, Q_1. Under these conditions the whole of the chlorine introduced at the outset, is at the end, and in a moment, changed into hydrochloric acid, as can be easily proved. The final as well as the initial state is therefore completely definite. The sum

$$Q + q + Q_1$$

represents the total heat liberated during the passage from the initial to the final state; or, for $Cl_2 = 71$ grms.

$$\frac{Q + q + Q_1}{p} \times 71 = S.$$

The heat liberated, from the initial to the final system, is therefore $69 + S$.

But we could have passed from the same initial to the same final state according to the following succession—unite 2H with 2Cl, forming 2HCl dilute, liberating + 78·6 Cal.; then unite nHCl dilute with nBaO dissolved, forming $nBaCl_2$ dissolved, which liberates + 13·85n; lastly unite O_2 gaseous + $Ba(NO_2)_2$ dissolved, which produces $Ba(NO_3)_2$ dissolved, liberating x. The thermal sum being the same in both processes, we have the equation—

$$S - 13{\cdot}85n - (78{\cdot}6 - 69) = x.$$

Three concordant experiments, made according to this process, each on about 2 grms. of nitrite, yielded

$$x = 22{\cdot}1 \text{ Cal.},$$

a value which corresponds to the following reaction, $Ba(NO_2)_2$ dissolved + O_2 gas = $Ba(NO_3)_2$ dissolved. The precautions employed in these experiments to avoid the use of gaseous chlorine, either in a neutral or acid medium, and also against the sudden transformation of the chlorine into chloride, or the variable formation of oxides of chlorine, should be observed;[1] free hypochlorous acid has also been included, because this acid is difficult to obtain quite free from chlorine or the higher oxides of chlorine, besides, it decomposes spontaneously, and also in presence of bodies which it oxidises, especially in an acid medium.[2]

Second process. Barium dioxide.—The barium nitrite is changed into nitrate by barium dioxide dissolved in hydrochloric acid. $Ba(NO_2)^2$ dilute + $2BaO_2$ + 4HCl dilute = $Ba(NO_3)_2$ dilute + $2BaCl_2$ dilute + $2H_2O$.

The initial system is the following:—

$Ba(NO_2)_2$ dilute, 2BaO anhydrous; O_2 gas; 4HCl dilute, all these bodies being separate.

The final system is the following:—

$Ba(NO_3)_2$ dilute, $2BaCl_2$ dilute + $2H_2O$.

[1] "Annales de Chimie et de Physique," 5e série, tom. v. p. 322.
[2] Ibid., p. 342.

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We may pass from one to the other by following two different cycles.

FIRST CYCLE.

$Ba(NO_2)_2$ dilute + O_2 = $Ba(NO_3)_2$ dilute	x
$2BaO_2$ anhydrous + 4HCl dilute = $2BaCl_2$ dilute + $2H_2O$	+ 55·58
Sum	+ 55·58 + x

SECOND CYCLE.

$2(BaO + O)$ = $2BaO_2$ anhydrous	+ 12·1
$2BaO_2$ + 4HCl dilute, then reaction of this solution on dissolved $Ba(NO_2)_2$	R
Sum	R + 12·1

R being determined by experiment it is easy to calculate x. The experiment is carried out as follows:—

A known weight, p, of anhydrous barium dioxide, say 8·5 grms. for example, is dissolved in the calorimeter by dilute hydrochloric acid; the quantity of heat liberated, Q, is measured. With 8·50 grms. it is practically equal to $\frac{11·0}{20}$ Cal. To the liquid is then added a quantity of barium nitrite strictly equivalent to the barium dioxide employed, or 6·20 grms. The nitrite should be dissolved beforehand in twenty-five times its weight of water, and the temperature of the solution accurately measured a moment before it is mixed in the calorimeter with the hydrochloric acid and solution of barium dioxide. Immediately upon this mixture being effected, several phenomena are produced and succeed each other rapidly, the solution becomes yellow, then for a moment it becomes turbid, as if a precipitate were forming; a few excessively fine gaseous bubbles appear for an instant without giving rise to the production of an appreciable volume of gas; then the liquor becomes perfectly clear. A minute, and even less, suffices for the accomplishment of all these effects.

At this point the liberation of heat is at an end, and the nitrite entirely changed into nitrate.

From the data observed is calculated the heat liberated during the last metamorphosis, say Q′.

Hence we have, calling E the equivalent of barium dioxide, BaO_2 = 84·5 grms. as the expression for the heat liberated.

$$R = \frac{Q + Q'}{p} E$$

therefore the heat liberated in the transformation of nitrite of baryta into nitrate will be

$$x = R + 12·1 - 55·58 = R - 43·5.$$

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Experimental results. First experiment at 12°—

$2BaO_2$ dissolved in 4HCl dilute	+ 22·02
Reaction on $Ba(NO_2)_2$ dissolved	+ 43·23
R =	+ 65·25

whence may be deduced

$$x = + 22{\cdot}25.$$

Second experiment at 12°—

In this experiment crystallised barium nitrite was directly dissolved in the hydrochloric solution of barium dioxide.

$2BaO_2$ + 4HCl dilute	+ 21·84
Reaction on crystallised $Ba(NO_2)_2H_2O$ ...	+ 38·75
Sum	+ 60·59

This experiment was purposely made with crystallised nitrite of baryta in order to vary the conditions. To make it comparable with the proceeding it is necessary to add to the number obtained the dissolving heat of the salt at the same temperature, taken with the contrary sign, viz. + 4·30.

Hence we have

$$R = + 64{\cdot}89$$

whence may be deduced

$$x = 21{\cdot}49$$

The two experiments have therefore given

22·25 and 21·49

or a mean of

21·87 or 21·9 Cal.

This is therefore the quantity of heat liberated in the following reaction:

$$Ba(NO_2)_2 \text{ dissolved} + O_2 \text{ gas} = Ba(NO_3)_2 \text{ dissolved.}$$

Third process. Liquid bromine.—The theoretical reaction is the following:—

$$Ba(NO_2)_2 \text{ dissolved} + Br_4 + 2H_2O = Ba(NO_3)_2 \text{ dissolved} + 4HBr \text{ dissolved.}$$

Pure liquid bromine is weighed in an hermetically sealed tube, say, for example, 2·254 grms. A strictly equivalent weight of pure barium nitrite is also weighed. The water is placed in the calorimeter, the salt is dissolved in it, and the tube introduced. When equilibrium of temperature is established the bromine tube is crushed, and the whole is quickly stirred.

The reaction of bromine on barium nitrite does not, however, take place so rapidly as in the case of chlorine; it does not completely dissolve until after some time, and the solution retains, even after twenty minutes, a strong odour of bromine. In a

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word, the nitrite and the bromine are not entirely changed into nitrate and hydrobromic acid under these conditions, but there exists in the solution a bromonitric compound analogous to aqua regia, and the continued presence of which interferes with the application of the calorimetric calculation by means of the equation given above.

As a matter of fact the calculation applied to the results of these experiments has given results falling below the theoretical reaction $Ba(NO_2)_2$ dissolved + O_2 = $Ba(NO_3)_2$ dissolved; the value obtained fluctuating about + 18 Cal. instead of + 22 Cal. These results are, therefore, not included in the averages on account of the incomplete nature of the transformation. But it has been thought proper to point out, from the purely chemical point of view, the true character of the reaction of bromine on the nitrites.

Fourth process. Potassium permanganate.—It is well known with what accuracy this reagent may be employed to convert nitrites into nitrates.

The experiments were performed with a solution of absolutely pure potassium permanganate of known strength,[1] mixed with a large excess of dilute sulphuric acid;[2] for instance, 192 cms. of the permanganate solution (20 grms. = 1 litre) and 1800 cms. of a solution of dilute sulphuric acid, mixed in a large platinum calorimeter and 2·470 grms. of crystallised barium nitrite, $Ba(NO_2)_2H_2O$, added. The reaction is instantaneous. The heat liberated is measured as soon as the reaction is accomplished, the excess of the permanganate is reduced by a standard solution of oxalic acid (160 cms. for instance), the whole of the carbonic acid formed remains dissolved. The quantities of heat liberated in this second reaction are also measured.

The sum of the quantities of heat which result from the foregoing experiments represents the heat liberated.

As a check, the excess of oxalic acid remaining in the liquid is ascertained. These measurements, combined with the data contained in the author's *Mémoire sur la chaleur de combustion de l'acide oxalique*,[3] and with the figures obtained in the reduction of potassium permanganate by oxalic acid,[4] enable us to calculate the heat liberated in the transformation of barium nitrite into nitrate.

Finally, by this method it was found that the reaction $Ba(NO_2)_2$ dissolved + O_2 gas = $Ba(NO_3)_2$ dissolved liberates—

First trial	...	...	...	...	...	+ 21·7 Cal.
Second trial	...	...	...	...	...	+ 20·5 „
			Mean	...	...	+ 21·1 „

These results are rather less reliable than those of the two

[1] "Annales de Chimie et de Physique," 5e série, tom. v. p. 306.
[2] Ibid., p. 308. [3] Ibid., p. 305. [4] Ibid., p. 309.

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first methods, owing to the complex nature of the thermal reactions of permanganate. Their mean, however, is sufficiently concordant.

To sum up, the reaction

$Ba(NO_2)_2$ dissolved + O_2 = $Ba(NO_3)_2$ dissolved liberates—

According to the results obtained with	gaseous chlorine	+ 22·1
" " " " "	barium dioxide	+ 21·9
" " " " "	potassium permanganate	+ 21·1
	Mean	+ 21·7

This value is applicable not only to the oxidation of barium nitrite, but also to the oxidation of all dissolved alkaline nitrites.

Hence from the knowledge of the heats of neutralisation of nitrogen trioxide (+ 10·6) and nitric acid (+ 13·8) by baryta:

N_2O_3 very diluted + O_2 + H_2O = $2HNO_3$ dilute liberates + 18·5 Cal.

For both the bodies gaseous we have, according to the data given further on:

N_2O_3 gas + O_2 = N_2O_5 gas liberates + 10·5 Cal.

Hence the change of the nitrogen trioxide into the pentoxide liberates, when the action takes place, upon the gases, + 10·5; on the dissolved bodies, + 18·5; lastly, in presence of alkalis, + 24·7. The great difference between the quantities of heat liberated by one and the same transformation, according to the state of the bodies, deserves attention, being due to the difference in the heats of hydration and neutralisation of the two acids.

We will also give here the heats of oxidation of the solid and anhydrous nitrites, which are easily calculated if their dissolving heat be known.

	Dissolved salts.	Solid salts.
$Ba(NO_2)_2 + O_2 = Ba(NO_3)_2$ liberates	+ 21·7	+ 23·5
$NH_4NO_2 + O = NH_4NO_3$ liberates	+ 21·8	+ 23·3
$AgNO_2 + O = AgNO_3$ liberates	+ 20·3	+ 17·2

3. Second method. By nitric acid and barium dioxide. A known quantity of concentrated and pure nitric acid is allowed to absorb dry nitric oxide, the weight of which is determined by a fresh weighing after having measured the heat liberated, say Q for NO = 30 grms. The concentrated acid is contained in a small tube, which is weighed and closed and plunged into the calorimeter throughout the whole duration of the absorption. A thermometer sensitive to $\frac{1}{200}$ of a degree gives the temperature of the calorimeter; a smaller thermometer,

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sensitive to $\frac{1}{20}$ of a degree, gives that of the acid, the latter being kept as near as possible to that of the calorimeter. The corrections for cooling are made according to the ordinary processes.[1] It is with the aid of all these data that the quantity, Q, is calculated. Further, a weight of anhydrous barium dioxide equivalent to the above weight of nitric oxide absorbed ($3BaO_2$ for 2NO) is dissolved in the excess of dilute hydrochloric acid, which liberates Q_1. The concentrated nitric acid, which has dissolved the nitric oxide, is then mixed in the calorimeter with the hydrochloric solution of barium dioxide. The whole is thus brought to the final state of dilute nitric acid and dilute barium chloride, liberating a measured quantity of heat equal to Q_2. Lastly is dissolved the same weight of the same pure nitric acid as used at the outset, in the same volume of dilute hydrochloric acid, which liberates a quantity of heat, P.

As a check, a weighed quantity of barium dioxide is added to the solution, which should, and in fact does, produce the same quantity of heat as if it were dissolved in a solution containing only hydrochloric acid; which proves that the nitric acid employed is very free from nitrogen trioxide.

This being established we have all the data for the calculation. Let the initial system be O_3; 2NO; 3BaO; $m(2HNO_3 + nAq)$; 6 HCl dilute; these bodies being taken separately; and let the final system be $3(BaCl_2 + H_2O$ dissolved $+ (m + 1)$ $2HNO_3$ dilute). We can pass from one to the other according to the two following cycles:—

First Cycle.

$3BaO + 3O = 3BaO_2$ anhydrous liberates	+ 18·0 Cal.
$6HCl$ dilute $+ 3BaO_2$	Q_1
Reaction of NO on the concentrated nitric acid ...	Q
Reaction between the two mixtures	Q_2
Sum	+ 18·0 Cal. + Q + Q_1 + Q_2

Second Cycle.

3BaO anhydrous + 6HCl dilute liberates + 27·8 × 3 (according to the author's experiments) or ...	+ 83·4 Cal.
$2NO + O_3$ + water = $2HNO_3$ dilute	x
$m(HNO_3 + nAq)$ + water	P
Sum	+ 83·4 Cal. + x + P

whence we deduce the value of x:

$$+ 18{\cdot}0 \text{ Cal.} + Q + Q_1 + Q_2 = + 83{\cdot}4 \text{ Cal.} + x + P.$$

The experiments gave $x = 34{\cdot}4$ Cal., a value which is slightly too small.

4. The third method is based on the use of nitric peroxide.

[1] "Essai de Mécanique Chimique," tom. i. p. 208.

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The results have been given above (pp. 168 to 171). They may be summed up as follows:—

$NO + O = NO_2$ gas	+ 19·4
Liquefaction of NO_2	+ 4·33
$2NO_2$ liquid + O + H_2O + water = $2HNO_3$ dilute ...	+ 12·7

We have therefore:

$$2NO + O_3 + H_2O + \text{water} = 2HNO_3 \text{ dilute} + 36{\cdot}4.^1$$

These results are worthy of attention, but they do not appear capable of great accuracy, owing to the uncertainty of the reactions.

5. To sum up the results of the different methods—

$NO + O_3$ + water = HNO_3 dilute: by the nitrites ...	+ 35·9
" " " " by nitric acid ...	+ 34·4
" " " " by nitric peroxide ...	+ 36·3
Mean	+ 35·5

However, the accuracy of the three methods is very unequal, so the value 35·9 will be adopted, the method by which it was obtained being most reliable, taking the two other figures as mere verifications.

6. *Heat of formation of dilute nitric acid from its elements.* This heat, calculated from nitrogen and oxygen, is easily deduced from the preceding results, for it is sufficient to deduct from the latter the heat absorbed in the formation of nitric oxide.

$$N_2 + O_5 + H_2O + \text{water} = 2\ HNO_3 \text{ dilute liberates} + 35{\cdot}9 - 21{\cdot}6 = + 14{\cdot}3 \text{ Cal.}$$

If we consider the integral formation of nitric acid from its three elements, HNO_3, we must add the heat of formation of water, viz. + 34·5. Thus $N_2 + O_5$ + water = $2HNO_3$ dilute liberates + 48·8 Cal. Such a reaction, therefore, liberates heat. Hence it can take place directly, and, in fact, it is observed in the combustion of the hydrogen in the air, but it only affects a small quantity.

7. *Heat of formation of nitric acid.* It is sufficient to measure the heat liberated by the solution of the liquid acid in a large quantity of water, viz. + 7·2. We have therefore—

$N_2 + O_5 + H_2O = 2HNO_3$ liquid liberates ...	+ 7·1
$N_2 + O_5 + H_2 = 2HNO_3$ " ...	+ 41·6

To pass from the gaseous to the solid state, it is sufficient to measure the heat of vaporisation and the heat of fusion at a low temperature of nitric acid, $HNO_3 = 63$ grms.

The result found for the heat of vaporisation is + 7·35, and for fusion —0·6.

[1] Thomsen, following an analogous though not identical cycle, found + 36·47.

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We have, therefore, neglecting the differences between the specific heats of the body under its various states—

$N_2 + O_5 + H_2O$ solid = $2HNO_3$ solid (at low temperature) ...	+ 7·0
$N_2 + O_5 + H_2$ „ = $2HNO_3$ „	+ 42·2
$N_2 + O_5 + H_2O$ gas = $2HNO_3$ gas	− 0·1
$N_2 + O_5 + H_2$ „ = $2HNO_3$ „	+ 34·4

8. *Acid at different degrees of concentration.* To pass to nitric acid regarded under different states of concentration, it is sufficient to know its heat of dilution, under its various states, and to add it to the foregoing figures. It has been measured for the whole scale of dilutions, and the results will be found in the "Annales de Chimie et de Physique," 5ᵉ série, tom. iv. p. 446. We confine ourselves to giving here the heat of formation of the hydrate HNO_3, $2H_2O$, which represents approximately the acid of commerce.

$$HNO_3 + 2H_2O = HNO_3{\cdot}2H_2O \text{ liquid, liberates } + 5{\cdot}0 \text{ Cal.}$$

Engravers' aqua fortis approaches the formula

$$HNO_3 + 6{\cdot}5H_2O.$$

The formation of such a hydrate,

$$HNO_3 + 6{\cdot}5H_2O = HNO_3\ 6{\cdot}5H_2O, \text{ liberates } + 7{\cdot}0.$$

9. *Nitrogen pentoxide,* N_2O_5. *Preparation.* It is well known that this body was discovered by Sainte-Claire Deville in the reaction of chlorine on silver nitrate. A more simple method was devised by the author. The principle of the process was discovered by Weber in 1872,[1] and consists in dehydrating nitric acid by phosphoric anhydride. Nitric acid, cooled by a freezing mixture, is mixed with pulverulent phosphoric oxide in small portions at a time, taking care to avoid any elevation of temperature. The temperature of the mass should never exceed 0°. When a little more than its weight of phosphoric oxide has been added to the nitric acid, the mass becomes of the consistency of a jelly. It is then placed in a roomy tubulated retort and distilled with extreme slowness. The products are condensed in receivers with ground stoppers, immersed in ice. In this way large, brilliant, colourless crystals of nitrogen pentoxide are obtained, which are perfectly pure. From 150 grms. of nitric acid nearly 80 grms. of the crystals were obtained. This substance is non-explosive either as a solid or in vapour. It decomposes, however, very easily, and this at the ordinary temperature, as Deville has observed, into nitric peroxide and oxygen. It should not be preserved in hermetically sealed vessels. It keeps well in good glass-stoppered bottles placed under a bell glass with sulphuric acid. In the air the crystals evaporate slowly, evolving abundant vapours, but not liquefying. Hence they can be weighed

[1] "Ann. Pogg.," tom. cxlvii. p. 113.

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without difficulty. Light accelerates its decomposition, as does also heat, though even at 43° it is not very rapid. This change into nitric peroxide and oxygen is endothermic, and is not reversible.

The following is the analysis of these crystals:—5·555 grms. of crystals weighed, and dissolved in water, yielded a solution which, according to alkalimetric test, contained 5·54 grms. of nitrogen pentoxide; no appreciable quantity of nitrogen trioxide was present (reaction of potassium permanganate). A large quantity having been prepared, its action on water in the calorimeter was studied, taking it successively under the three states, solid, liquid, and gaseous.

Solid state—

N_2O_5 crystallised + H_2O + water at 10° = $2HNO_3$ dilute + 8·34 Cal.

Now

$N_2O_5H_2O$ pure + water at 10° = $2HNO_3$ dilute liberates + 7·18 Cal.;

therefore

N_2O_5 solid + H_2O liquid = $2HNO_3$ pure and liquid liberates + 1·16 Cal.

This quantity of heat is very small, as might be expected, owing to the contrary thermal effect produced by the liquefaction of the anhydrides.

Hence, the action of the solid anhydride on water is not very violent, which confirms in another way the above result. The union of the solid anhydride with atmospheric aqueous vapour is likewise slower than that of bodies said to be very hygroscopic. In fact, at the ordinary temperature, the anhydride evaporates without leaving any appreciable quantity of dilute acid. The following reaction refers to the solid state—

N_2O_5 solid + BaO solid = $Ba(NO_3)_2$ solid liberates + 40·7.

This quantity of heat is less by + 10·3 than that liberated by the formation of barium sulphate starting from the anhydrous acid and the anhydrous base, both being solid, viz. + 51·0.

Liquid state.—Heat of fusion was determined by two methods:

(1) By the solidification of the dissolved acid contained in a tube, immersed in the calorimeter.

(2) By dissolving directly the solid acid in water.

The following figures result from determination of the above methods:—

N_2O_5 (=54 grms.) liquid, in becoming solid, liberates + 4·14, or, for N_2O_5 (=108 grms.), + 8·28.

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This value is very high and equal to about six times the heat of solidification of water (+ 0·72 for H_2O = 9 grms., according to Desains).

Therefore

N_2O_5 liq. + H_2O liq. = $2HNO_3$ liq. and pure liberates + 5·3 Cal.
N_2O_5 liq. + H_2O liq. + water = dilute acid + 12·48 Cal.

The first value is nearly but not quite equal to that of the heat of hydration of acetic anhydride ($C_4H_6O_3$ liquid + H_2O liquid = $C_4H_8O_4$ liquid liberates + 6·9), but the second is much greater than the heat of hydration of anhydrous acetic acid referred to the dilute acid (+ 7·3). Hence the action of the liquid nitrogen pentoxide on water is extremely violent in contrast with the very much weaker reaction which water exercises on the solid acid.

Gaseous state.—Heat of vaporisation. N_2O_5 gas, changed into liquid, liberates + 2·42, and into solid, + 6·56.

This quantity was determined by introducing dry air charged with nitrogen pentoxide vapour into the water of the calorimeter, at a temperature of 43°. The preliminary vaporisation of the pentoxide in the current of air was produced by means of a small air bath.

The decomposition of the pentoxide into the tetroxide and oxygen is not appreciable under these conditions of vaporisation.

Known weights of pentoxide, previously weighed in a sealed tube, have been operated on, the result being checked by the acidimetric test of the aqueous solution.

By this means is obtained the heat liberated when nitrogen pentoxide is changed into dilute acid, viz.

N_2O_5 gas + water = dilute acid, at + 10° liberates + 14·9.

The heat of vaporisation of the liquid acid is therefore for the weight—

$$N_2O_5 = 54 \text{ grms.}$$
$$14·9 - 12·48 = 2·42,$$

or, for (N_2O_5 = 108), 4·84 Cal.

That of the solid, for (N_2O_5 = 54 grms.)—

$$14·90 - 8·34 = 6·56,$$

or, for (N_2O_5 = 108 grms.), 13·12.

According to the above figures, the heat of vaporisation of the liquid nitrogen pentoxide (admitting $\frac{1}{2}N_2O_5$ = 2 vols.) will be for N_2O_5, 4·84. It is nearly the same as that of nitric peroxide at the same volume, or 4·3 for NO_2. It is also nearly the same as the heat of vaporisation of nitrogen monoxide, viz. 4·42 for N_2O, according to Favre.

The thermal formation of nitrogen pentoxide from the elements

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is deduced from the foregoing data. Under the three states we have—

$N_2 + O_5 = N_2O_5$ gas ... ... + 0·6
$N_2 + O_5 = N_2O_5$ liquid ... ... + 1·8
$N_2 + O_5 = N_2O_5$ solid ... ... + 5·9

10. The following table shows the thermal formation of the oxides of nitrogen under the gaseous form, referred to the ordinary temperature:—

$N_2 + O = (2v.)N_2O - 10·3$ } − 11·3
$N + O = (4v.)NO - 21·6$ }
+ 10·5
$N_2 + O_3 = (2v.)N_2O_3 - 11·1$ }
+ 8·5
$N + O_2 = (4v.)NO_2 - 2·6$ }
+ 2·0
$N_2 + O_5 = (2v.)N_2O_5 - 0·6$

It will be seen that the progressive formation of the oxides of nitrogen follows a peculiar course. It first absorbs a quantity of heat nearly proportional for the first two, then liberates quantities which go on decreasing. These bodies are here given under the gaseous form, the only one which is really comparable. The most stable compound, nitric peroxide, corresponds neither to the maximum nor to the minimum of the heat absorbed. In short, there exists no simple numerical relation between the quantities of heat brought into action.

The most general fact, following from the foregoing table, is that the formation of all the oxides of nitrogen from their gaseous elements absorbs heat, their decomposition must therefore liberate it. Nevertheless not one of them is explosive by simple heating. But nitric oxide, formed with the greatest absorption of heat, is decomposed into its elements with facility, as will be established further on (see p. 191). The heat absorbed in its formation renders it comparable to cyanogen (−37·3 for C_2N_2) or to acetylene (−30·5 for C_2H_2). These three bodies can, moreover, undergo a true explosion under the influence of the sudden and violent shock of mercury fulminate (p. 66). These three bodies indicate an aptitude for combination altogether comparable to that of the simple radicals. Hence from a knowledge of these relations may be understood why the formation of the oxides of nitrogen never takes place directly, and why it requires the aid of a foreign energy, such as electricity, or of a simultaneous chemical action.

It also explains the great energy of explosive mixtures and compounds formed by the oxygen compounds of nitrogen.

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§ 7. Hyponitrous Acid and Hyponitrites.

1. In studying the products of the reduction of the nitrates by sodium amalgam, Divers[1] discovered in 1871 a new salt, which he called silver hyponitrite, and of which he determined the composition and the properties. This salt and its derivatives have since been the object of researches by Van der Plaats[2] and Zorn.[3] These chemists have attributed to silver hyponitrite the formula AgNO, which would suppose it derived from nitrogen monoxide, associated with silver oxide. But the recent researches which Ogier and the author have made upon this salt from a chemical and thermal point of view have led them to prefer the formula $Ag_4N_4O_5$, that is to say $2Ag_2O,N_2O_3$, which makes of the hyponitrous acid a sesquioxide of nitrogen.

The alkaline hyponitrites are also formed in the electrolysis of the nitrites, and they are formed, though to a very small amount, in the decomposition of the nitrites by heat, especially in presence of iron. It is by means of silver hyponitrite that hyponitrous acid and its salts are prepared; we shall speak, therefore, first of all, of this compound.

2. Silver hyponitrite is a yellow amorphous very insoluble body, which is precipitated when silver nitrate is poured into a neutral solution of alkaline nitrite. In order to obtain it pure, it must be re-dissolved in very dilute nitric acid, and re-precipitated, by neutralising by ammonia.

This body undergoes a very sensible decomposition when heated to 100° or a little over.

Hence the hyponitrite should be dried in vacuo at the ordinary temperature, and in the dark.

Its analysis has supplied the following figures:—

Ag	...	...	...	...	76·2	...	...	76·1
N	...	...	...	...	9·7	...	...	9·8
O	...	...	...	...	14·1	...	...	14·1

These results lead to the formula—

	Calculated from AgNO(138)		½$Ag_4N_4O_5$(284)		Found.
Ag	78·3	...	76·1	...	76·1
N	10·1	...	9·9	...	9·8
O	10·6	...	14·1	...	14·1

Hyponitrous acid has therefore as formula $N_4O_32H_2O$, which constitutes it a sesquioxide of nitrogen, corresponding in the anhydrous state to the formula N_4O_3.

[1] "Journal of the Chemical Society," vol. xxiv. p. 484; "Proceedings of the Royal Society," vol. xxii. p. 425; "Bulletin de la Société Chimique," tom. xv. p. 176.

[2] "Berichte der Deutsch. Chem. Ges. Ber.," tom. x. p. 1508.

[3] Ibid., tom. x. p. 1306, and tom. xv. p. 1258.

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This formula accounts for the existence of the acid salts, observed by Zorn.

Silver hyponitrite is decomposed by heat, with formation of nitric oxide, nitrogen trioxide, and metallic silver—

$$Ag_4N_4O_5 = 2NO + N_2O_3 + Ag_4.$$

But the nitrogen trioxide reacts partially upon the silver, so as to reproduce a certain quantity of nitrite, and even nitrate of silver.

3. By decomposing silver hyponitrite by a dilute acid, hyponitrous acid is obtained in an aqueous solution. This acid is not at all stable. Its solutions raised to boiling point are decomposed, yielding nitrogen monoxide mixed with nitrogen, retaining at the same time a certain quantity of dilute nitric acid—

$$4N_4O_3 \text{ dilute} + H_2O = 7N_2O + 2HNO_3.$$

On contact with the air they absorb oxygen slowly, becoming changed into nitric acid.

4. We have, with a view to calorimetric tests, methodically subjected hyponitrous acid to the action of the three following oxidising bodies—iodine, bromine, and potassium permanganate.

(1) A solution of iodine in potassium iodide did not exert any appreciable action on the hyponitrous acid combined with the silver[1] or previously liberated by an equivalent quantity of dilute hydrochloric acid.

(2) The oxidation by bromine is very characteristic. A known weight of silver hyponitrite, 2 grms., was mixed with hydrochloric acid in excess, and an aqueous solution of bromine, also slightly in excess, the strength of which was determined; the reaction was allowed to go on for some time, when the excess of bromine was determined. This method tends to give rather high figures, owing to the evaporation of some traces of bromine.

Or the hydrochloric acid may be mixed beforehand with bromine water in which salts of silver have been dissolved (series I.); or the salt dissolved in the acid and the bromine added (series II., p. 187).

The equivalent ratio between the silver and bromine employed has been found to be very nearly 1 : 3·5, which agrees with the formula.

$$Ag_4N_4O_5 + 7H_2O + 14Br = 4HNO_3 + 10HBr + 4AgBr.$$

The formula AgNO would require the ratio 1 : 4, which is greatly higher than all the quantities observed.

(3) The oxidation by potassium permanganate gives rather irregular results, the oxygen absorbed varying from 4·6 to 8·9 per cent., and the action going on almost indefinitely. However,

[1] Except the conversion of the silver into iodide.

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by operating in presence of a very great excess of sulphuric acid more concordant results may be obtained, such as 8·3; 7·5; 8·4; 8·9.

These figures correspond sensibly to three equivalents of oxygen absorbed.

The solutions do not contain ammonia, but liberate by ebullition a considerable quantity of nitrogen monoxide. In another experiment, the oxygen absorbed and the nitrogen monoxide were ascertained by analysis. The following results were obtained:—

O fixed : 8·3 :: N_2O liberated : 8·0 per 100 parts of salt.

These figures correspond very sensibly to the following transformation:—

$$Ag_4N_4O_5 + O_3 + H_2O = N_2O + 2HNO_3 - 2\,Ag_2O \text{ combined with the acid.}$$

This is therefore a fresh confirmation of the formula. The analysis by the permanganate must be made by introducing the salt of silver in a body into the mixture of permanganate and sulphuric acid made beforehand and in excess, as the hyponitrous acid set free slowly absorbs the oxygen of the air.

These facts being established, we have proceeded to the calorimetric measurements, and successively determined the heat of formation of the salt of silver, that of the acid itself, as well as the heat liberated by its union with silver and potassium oxides.

5. Heat of formation of silver hyponitrite. We determined the heat of formation of silver hyponitrite by oxidising it with bromine water in accordance with one of the foregoing experiments.

The figures obtained are sufficiently close. The following is a list of them:—

First Series.—Action effected by a single operation for Ag = 108 grms.

First	...	...	... 29·83 Cal.	mean 30·68.
Second	...	...	... 31·54 „	

Second Series.—Successive actions of HCl and Br.

Third	...	...	... 28·00 Cal.	mean 28·62.
Fourth	...	...	... 29·85 „	
Fifth	...	...	... 28·00 „	

The general mean of both series is equal to 29·65 Cal.

The experimental ratio between the silver and the bromine absorbed in equivalents was found to have a mean value of 3·71; a figure which is rather too high, owing, as before stated, to the loss of bromine by evaporation. The theoretical ratio is 3·50. Let therefore the initial system be $Ag_4N_4O_5 + 7H_2O +$

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14Br (gas) + water, the final state is arrived at by the following cycle:—

$$N_4 + O_5 + Ag_4 = N_4O_5Ag_4.$$

$7(H_2 + O) = 7H_2O$ liberates + 34·5 × 7 ...	= 241·5
4Br gaseous + water = 14Br dissolved ...	+ 29·0
Reaction (for Ag_4)	+ 59·3
	x + 329·8

the final state being—

$$2HNO_3 \text{ dilute} + 10HBr \text{ dilute} + 4AgBr.$$

The same final state may be arrived at by the following cycle:—

$2(H + N + O_3)$ + water = $2(HNO_3)$ dilute ...	+ 97·6
10(H + Br gas) + water = 10HBr dilute ...	+ 167·5
4(AgBr gas) = 4AgBr	+ 55·4
	+ 320·5

Both thermal sums being equal, it follows that

$$x = -9{\cdot}3 \text{ Cal.}$$

This is the heat absorbed in the reunion of the elements

$$Ag_4 + N_4 + O_5.$$

We have further, starting with nitrogen, oxygen, and silver oxide—

$$2Ag_2O + N_4 + O_{3?} - 16{\cdot}3 \text{ Cal.}$$

6. Heat of formation of hyponitrous acid. To pass to the acid itself, we measured the heat liberated in the reaction of dilute hydrochloric acid on silver hyponitrite, viz. for one equivalent of silver, Ag, contained in this compound.

$$\left.\begin{matrix} + 9{\cdot}15 \text{ Cal.} \\ + 8{\cdot}73 \text{ ,,} \end{matrix}\right\} \text{mean} + 8{\cdot}94 \text{ Cal.}$$

which makes for Ag_2 + 17·88.

The hyponitrous acid exists, moreover, after this operation, or at least throughout the duration of the experiment, as is shown by the agreement of the estimations of bromine effected before and after the action of the hydrochloric acid.

This being established, the reaction

$$2HCl + Ag_2O = 2AgCl + H_2O \text{ liberates} + 20{\cdot}1;$$

whence it follows that

$$N_4O_3 \text{ dilute} + 2Ag_2O = Ag_4N_4O_5 \text{ liberates} + 40{\cdot}2 - 17{\cdot}9 = +22{\cdot}3,$$

or + 12·15 for each equivalent of oxide combined. Hence we have $N_4 + O_3$ + water = N_4O_3 dilute − 38·6 Cal. Hyponitrous acid is therefore formed from its elements with absorption of heat, as would be supposed from the instability of the acid itself.

Its transformation into nitric acid, by oxidation (by means of bromine), liberates N_4O_3 dilute + O_7 + $2H_2O$ = $4HNO_3$ dilute

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+ 67·2 or + 9·6 Cal. per equivalent of oxygen fixed. This figure is hardly higher than that obtained for the transformation of dissolved nitrous acid into dilute nitric acid. N_2O^3 dilute + O_2 + H_2O = $2HNO_3$ dilute + 18·15, or 9·25 cal. for each O fixed. However, if we regard the two successive oxidations, the calculation shows that the oxidation of the nitrogen trioxide forming nitrous acid liberates a little more heat, viz. 10·1 per O fixed, than that of the nitrous acid changed into nitric acid, viz. 9·25. The change even of one of the salts into the other would liberate, for solid salts of silver—

Hyponitrite changed into nitrite per O fixed + 10·4.
Nitrite into nitrate + 8·8.

For the dissolved salts of potassium the difference is increased, owing to the difference in the heats of neutralisation.

Hyponitrite changed into nitrite per O fixed + 13·6.
Nitrite into nitrate + 10·8.

The relations are always of the same kind.

7. The oxidation by permanganate, with formation of nitrogen monoxide (deducting the heat due to the reduction of the permanganate)—

N_4O_3 dil. + O_3 + H_2O = $2HNO_3$ dil. + N_2O gas liberates + 42·3.

The slow decomposition of the hyponitrous acid in contact with the air, and at the expense both of the free oxygen and that dissolved in the water, liberates exactly the same quantity of heat with formation of nitrogen monoxide. The pure and simple separation N_4O_3 dil. = 2NO + N_2O gas would liberate + 6·4. The nitrogen monoxide can moreover be formed without nitric acid by other methods, which liberate much more heat, and are therefore preferable—

$7N_4O_3$ + water = $7N_2O$ gas + $2HNO_3$ dil. liberates + 96·6,

or + 24·1 for N_4O_3. Combinations of hyponitrous acid present a mobility and complexity of reactions which are explained by their endothermal formation. Many analogous phenomena are known in the series of the lower oxides of sulphur and phosphorus, not to speak of hydroxylamine, which also very easily yields nitrogen and nitrogen monoxide.

8. The heat of neutralisation of dilute hyponitrous acid by silver oxide has been given above, viz.

$$N_4O_3 \text{ dilute} + 2Ag_2O_4 = Ag_4N_4O_5 + 11{\cdot}15 \times 4.$$

We have tried also to estimate the heat of neutralisation of hyponitrous acid by the alkalis, by decomposing salts of silver by the alkaline chlorides. The reaction is almost instantaneous. We obtained $\frac{1}{2}(Ag_4N_4O_5 + 4HCl)$ dilute at about 14° + 5·50 Cal. With barium chloride, $BaCl_2$, the liberation of heat has been more considerable, but it seems to be complicated by the

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partial precipitation of barium hyponitrite. With ammonium chloride there is produced a special decomposition, setting free ammonia, which has already been observed by Divers. According to the above figures, we have, for potash and hyponitrous acid at 14°—

N_4O_2 dilute + $2K_2O$ dilute liberates $2(+ 8{\cdot}9 + 13{\cdot}8 + 2{\cdot}75 - 20{\cdot}1) = + 2 \times 5{\cdot}35$ Cal.

Let us now compare these results with the analogous numbers relating to the two other acids of nitrogen—

$\frac{1}{2}$($2HNO_3$ dilute + Ag_2O, forming $2AgNO_3$) solid...	+ 10·7 Cal.
$\frac{1}{2}$(N_2O_3 dilute + Ag_2O, forming $2AgNO_2$) solid ...	+ 12·1 „
$\frac{1}{4}$(N_4O_2 dilute + 2 Ag_2O, forming $Ag_4N_4O_6$) ...	+ 11·1 „

These are nearly the same values as for silver oxide forming solid salts. For potash, on the contrary, forming soluble salts—

$\frac{1}{2}$($2HNO_3$ dilute + K_2O dilute)	+ 13·8 Cal.
$\frac{1}{2}$(N_2O_3 dilute + K_2O dilute)	+ 10·6 „
$\frac{1}{4}$(N_4O_2 dilute + $2K_2O$ dilute)	+ 5·4 „

The relative weakness of the latter acids, a weakness which is correlative with their decreasing percentage of oxygen, is here more and more marked.[1]

§ 8. Stability and Reciprocal Reactions of the Oxygen Compounds of Nitrogen.

1. The carrying out of so many thermal determinations has led to the study of the formation and decomposition of the various oxides of nitrogen, a subject which had not been reconsidered since the time of Gay-Lussac,[2] Dulong,[3] Dalton,[4] and Priestley. Some of Peligot's[5] famous experiments on nitric peroxide and nitrogen trioxide have also been repeated.

The results obtained were unexpected, and contrary to the received opinions on the stability of nitric oxide.

2. *Nitrogen monoxide*, according to Priestley, is decomposed at

[1] We think it well to give here the calculation of the heats of formation of the hyponitrites according to the old formula. The calculation can only be effected upon the supposition that the oxidation by the bromine should not be quite complete, 3·71 equivalents of oxygen having been fixed instead of 4, which is equivalent to admitting that the action of the bromine should have liberated + 30·65 Cal. per equivalent of silver (taking into account the formation of AgBr, which is not changed). We thus find—

$\frac{1}{2}$($N_2 + O_2 + AgBr = 2AgNO$)	− 8·25
$N_2 + O +$ water $= N_2O$ dissolved	− 22·90
N_2O dissolved + $Ag_2O = 2AgNO$ precip.	+ 11·15
N_2O dissolved + $K_2O = 2KNO$ dissolved ...	+ 5·35

The deductions and general points of similarity remain moreover the same.

[2] "Annales de Chimie et de Physique," tom. i. p. 394. 1816.

[3] Ibid., tom. ii. p. 517. 1816.

[4] Ibid., tom. vii. p. 36. 1817.

[5] Ibid., 3e série, tom. ii. p. 58. 1841.

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a red heat, or by the electric spark, into nitrogen and oxygen. This decomposition is the easier, as it liberates heat.

$$N_2O = N_2 + O + 10{\cdot}3 \text{ Cal.}$$

In this way, it is not accompanied by dissociation, and is not, therefore, reversible.

Experiments were made with a view of determining at about what temperature this decomposition commences, and if nitric oxide were produced. The monoxide resists the action of a moderate heat better than is generally supposed. By heating it to a dull red, about 520°, for half an hour, in a tube of Bohemian glass hermetically sealed, hardly 1·5 per cent. is decomposed into nitrogen and oxygen. The decomposition is, therefore, extremely slow. Let us note here that the transformation of nitrogen monoxide into nitric oxide at the ordinary temperature,

$$N_2O = N + NO, \text{ would absorb } - 1{\cdot}0 \text{ Cal.}$$

The sudden compression of nitrogen monoxide in an apparatus analogous to the gas tinder box (*briquet à gaz*) and under conditions capable of causing the explosion of a mixture of hydrogen and oxygen only produces traces of decomposition.

Nitrogen monoxide, mixed with oxygen and brought to a dull red heat in a sealed tube, does not yield nitric oxide, which is intelligible, its formation absorbing heat: $\frac{1}{2}(N_2O + O = 2NO)$ would absorb − 11·3. Finally, it must be remembered that nitrogen monoxide does not exert an oxidising action in the cold upon any known body, and that it is neither absorbed nor decomposed by alcoholic or aqueous potash.

The action of the electric spark on nitrogen monoxide was examined principally in order to study its first phases, for the general products have already been noted by Priestley, Grove, Andrews and Tait, as well as by Buff and Hoffmann. The experiment was made in a sealed tube in order to avoid any secondary action, from water or mercury.

Decomposition takes place rapidly, and nitrous vapour is immediately formed. One-third of the gas was decomposed within a minute. The decomposed part was divided in nearly equal proportions between the two following reactions:—

$$N_2O = N_2 + O.$$
$$4N_2O = N_2O_4 + 6N.$$

The first action may be regarded as especially due to the action of the heat of the spark; the second to the heat and electricity combined. Further, both reactions are exothermal: the first liberating + 10·3 Cal., and the second + 38 Cal., that is to say + 9·5 Cal. for every equivalent of nitrogen monoxide decomposed. At the end of three minutes, with stronger sparks (six Bunsen elements), nearly three-quarters of the gas was

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decomposed; always in the same manner, the second reaction slightly prevailing. Hence it will be seen that nitric oxide does not and cannot appear in the electric decomposition of the monoxide, since the latter always gives rise to an excess of free oxygen.

The proportion of nitric peroxide, formed in these experiments, represented nearly one-seventh of the final volume, a proportion which cannot be very far removed from that corresponding to the final equilibrium produced by the spark in an equivalent mixture of free nitrogen and oxygen, according to experiments detailed further on.

3. *Nitric oxide.* This gas is reputed one of the most stable. It has, however, been taught that the spark (Priestley) or the action of a red heat (Gay-Lussac) slowly decomposes nitric oxide into nitrogen or nitric peroxide, and that in the presence of mercury or iron there remains nothing but nitrogen (Buff and Hoffmann, 1860).

These opinions do not appear to be well founded. Nitric oxide[1] contained in a sealed glass tube and brought to a dull red heat, about 520°, commences to decompose. At the end of half an hour, the volume of the gas decomposed amounts to nearly the quarter of the initial volume. The decomposed portion was partly broken up into nitrogen monoxide and oxygen—

$$2NO = N_2O + O, \text{ a reaction liberating } + 11{\cdot}3 \text{ Cal.},$$

and partly into free nitrogen and oxygen—

$$2NO = N_2 + O_2, \text{ a reaction liberating } + 21{\cdot}6.$$

The first reaction, that is the formation of nitrogen monoxide, was predominant; but the oxygen, gradually regenerated in presence of an excess of non-decomposed nitric oxide, had partially transformed it, at first, into nitrogen trioxide—

$$2NO + O = N_2O_3 \text{ liberates } + 10{\cdot}5;$$

the total reaction,

$$4NO = N_2O + N_2O_3, \text{ liberating } + 21{\cdot}7.$$

Then, the oxygen increasing owing to a more advanced decomposition, nitric peroxide is formed—

$$2NO + O_2 = 2NO_2 \text{ liberates } + 19{\cdot}0;$$

the total reaction, that is to say

$$4NO = N_2 + 2NO_2, \text{ liberating } + 40{\cdot}6 \text{ Cal.}$$

[1] This gas was prepared by the reaction of nitric acid on a boiling solution of ferrous sulphate; it is the only reaction which yields it quite pure. The use of copper and nitric acid, even very dilute and cold, always gives rise to monoxide of which the proportion, variable with the length of duration of the reaction, may amount to more than a tenth of the volume of the gas disengaged.

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Another experiment, lasting six hours, under the same conditions, gave sensibly the same results, the proportion of nitric oxide decomposed being the same, and of monoxide rather less, but always very considerable. The action of the electric spark confirms and extends these results. It commences to exert itself with extreme promptitude, and presents several successive terms which deserve attention.

Operating upon the gas enclosed in sealed tubes with rather weak sparks (two Bunsen elements) a sixth of the gas was already decomposed at the end of one minute. The proportion would certainly have been larger, if the platinum electrodes were situated in the centre of the mass instead of being at the extremity, which retarded the mixture of the gases. About a third of the decomposed product consisted of nitrogen monoxide—

$$4NO = N_2O + N_2O_3,$$

the other two-thirds producing nitrogen and nitric peroxide—

$$4NO = N_2 + 2NO_2.$$

At the end of five minutes three-quarters of the nitric oxide was decomposed with formation of nitrogen monoxide and nitrogen trioxide and nitric peroxide. The ratio between the nitrogen monoxide and the nitrogen, that is, between the two modes of decomposition, was nearly the same as above. It is further necessary to distinguish between the calorific action of the spark, which causes the formation of monoxide (a body not formed by the spark acting on the elements), as well as of a portion of free nitrogen, and the action peculiar to electricity, as shown by an experiment of longer duration.

In fact, the flow of sparks prolonged for an hour leaves nothing but a mixture of non-decomposed nitric oxide (thirteen per cent. of the initial volume), nitrous vapour (more than forty per cent.), and nitrogen. But no appreciable quantity of monoxide was discovered. This gas therefore disappears before the nitric oxide, doubtless under the influence of the high temperature of the spark.

This fact, in apparent contradiction to the initial transformation of a part of the nitric oxide into monoxide, seems to show that the nitric oxide commences to undergo decomposition at a lower temperature than the monoxide, and that it nevertheless lasts, in part, longer, or at a higher temperature, in presence of the products of its decomposition.

However, the still more prolonged action of electricity causes it to disappear in its turn, at the same time that it diminishes the volume of the nitrous vapour produced in the first period. After eighteen minutes only twelve per cent. of nitrous vapour formed, solely of nitric peroxide. The gaseous mixture con-

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tained N = 44, O = 37, NO_2 = 13 for 100 volumes of the original gas.

On account of the duration of the reaction, and of the antagonistic influence tending to the formation of nitric peroxide, in a mixture of pure nitrogen and oxygen traversed by the spark, the above system must be regarded as nearly in a state of equilibrium.

But to return to the nitric oxide. On the whole this compound is less stable under ordinary conditions than the monoxide, since it is capable of producing it by decomposition under the influence of heat or the spark. Here an apparent contradiction between the known properties of the two gases manifests itself. Why do carbon, sulphur, phosphorus, when once ignited, continue to burn more easily in the monoxide than in the nitric oxide, a circumstance which has caused until now a greater stability to be attributed to the latter gas? The explanation is the following (see pp. 62 and 63): on the one hand, nitric oxide does not contain more oxygen at equal volumes than the monoxide, and, on the other hand, this oxygen only becomes available in totality for combustion at a much higher temperature, the nitric oxide being at first changed to a great extent into nitric peroxide, a body really more stable than nitrogen monoxide. The combustive energy of the nitric oxide, at the temperature of incipient red heat, must therefore be less than that of the monoxide, which is immediately resolved into nitrogen and free oxygen.

We have explained in the same way the impossibility of exploding a mixture of nitric oxide and hydrogen, or carbonic oxide. The combustion produced at the point of contact with the incandescent body, or on the path of the spark, does not raise the temperature to the degree requisite for the decomposition of nitric peroxide, whilst explosive mixtures liberating far more heat, as is the case with cyanogen and ethylene, explode with extreme violence.

The want of stability of nitric oxide is equally manifested in a number of slow reactions, carried out with the pure gas at the ordinary temperature, whether it be resolved into nitrite and monoxide under the influence of potash (Gay-Lussac)—

$$4NO + K_2O \text{ dilute} + \text{water} = 2KNO_2 \text{ dissolved} + N_2O \text{ liberates} + 39{\cdot}2 \text{ Cal.},$$

or whether it gradually oxidise various mineral bodies in the cold, according to the early observers, or certain organic compounds, according to the author's own experiments.[1]

The latter reactions take place in various ways. Sometimes the whole of the nitrogen of the nitric oxide is set free, liberating + 21·6 more than the heat produced with free oxygen.

[1] "Chimie organique fondée sur la synthèse," tom. ii. p. 485.

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Sometimes half the nitrogen only is set free, a slow reaction observable with essence of turpentine or benzene, which leave a residuum of nitrogen equal to the fourth of the volume of the nitric oxide. Sometimes nitrogen monoxide is set free, another slow reaction observable with sodium sulphide or stannous chloride, which leave nitrogen monoxide and nitrogen in equal volumes.

Sometimes even ammonia is set free, with the aid of the hydrogen of water, or various organic compounds.

Nitrogen monoxide, nitrogen, and ammonia are formed from the same causes in the greater number of reactions where an oxidisable body tends to bring nitric acid to the state of nitric oxide. Hence the latter gas, prepared by the reaction of the metals on dilute nitric acid, is seldom pure.

A similar tendency to slow and multiple decompositions is the distinctive character of unstable compounds formed with absorption of heat. Nitric oxide is comparable, under this head, with cyanogen and acetylene. Now, all these endothermal compounds have a capacity for entering into reaction, a sort of chemical plasticity very superior to that of their elements, and comparable to that of the most active radicals, a circumstance which may be explained by the excess of energy stored up in the act of their synthesis.

The potential energy of the elements generally diminishes in the act of combination; acetylene, cyanogen, and nitric oxide, however, form exceptions. There is no doubt some relation between this increase of energy and the capacity possessed by these compound radicals for entering directly into new combinations with the elements.

Under the influence of electricity we obtain the direct, though always endothermal reunion of the elements which form either acetylene itself or the hydrogenated combination of cyanogen, or the super-oxidised combination of nitric oxide.

4. *Nitrogen trioxide.* Let us first note the following thermal relations concerning anhydrous nitrous acid:

$$N_2O_3 = 2NO + O \text{ would absorb } - 10{\cdot}5 \text{ Cal.}$$
$$N_2O_3 = 2NO_2 \text{ liberates } + 8{\cdot}5.$$

Hence it follows that the breaking up of nitrous acid into nitric oxide and peroxide,

$$N_2O_3 = NO + NO_2, \text{ would absorb } - 2{\cdot}0 \text{ Cal.}$$

In fact, the three bodies contained in the last equation constitute a system in the state of dissociation, a system of which the equilibrium varies with the relative proportions, temperature, condensation, etc.

Gay-Lussac observed that oxygen and nitrogen, mixed in volumes in the ratio of 1 : 4 in the presence of a concentrated solution of potash, yield only nitrite.

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The same reaction occurs, *whatever be the relative proportions of the two gases and the order of the mixture*, in presence of concentrated alkaline solutions, and even of baryta water. Not only do the ratios between the volumes of the gases establish this fact, but analyses made on several grammes of matter have shown that the proportion of nitrogen trioxide formed corresponds to 96 or 98 per cent. of the nitric oxide employed.

If the reaction occur without proper precautions being taken to absorb the nitrogen trioxide, and particularly if it be executed with anhydrous bodies, nitric peroxide is formed.[1] Nitrogen trioxide acid cannot exist for any length of time except in the presence of the products of its decomposition. It is this complex mixture, variable according to circumstances, which constitutes the body called nitrous vapour, whenever oxygen is not in excess. The same remark applies, moreover, to the liquid acid, the purest nitrogen trioxide which has been obtained (Fritzche; Hasenbach), containing about one-eighth of nitric peroxide, according to the analyses. Peligot has for long insisted on this circumstance.

In presence of an excess of oxygen, there is formed, or rather there exists, only nitric peroxide, as is known from the labours of Gay-Lussac, Dulong and Peligot, who obtained in this way the crystallised acid. We will not dwell further on this point, except to observe that, nitrogen trioxide being the initial product of the reaction, even in presence of an excess of oxygen, we are forced to admit that nitric peroxide results from this nitrogen trioxide, combined afterwards with a second equivalent of oxygen—

$$N_2O_3 + O = 2NO_2.$$

In a dry gaseous mixture, as well as in presence of water, the formation of the two oxides takes place almost instantaneously. Admitting, according to analogy, and in conformity with an approximate gaseous density given by Hasenbach, that the formula N_2O_3 represents two volumes, the second reaction would offer this remarkable character, hitherto unique in the study of direct actions, of a real gaseous combination accompanied by increase of volume, three volumes of the component gases furnishing four volumes.

[1] The experiments were made with a system of two concentric bulbs (see p. 168) of known capacity, hermetically sealed, one containing dry oxygen, the other dry nitric oxide, about 300 to 400 cms. The inner bulb is broken, by a jerk, and the two gases are allowed to react. When the reaction is complete, the point of the outer bulb is broken in a solution of potash of known strength; the nitrogen trioxide and nitric peroxide are absorbed without affecting the nitric oxide. The nitrogen trioxide is absorbed without change, as proved by the foregoing tests. Nitric peroxide in the state of vapour is likewise completely absorbed, being changed according to a well-known reaction into nitrogen trioxide and nitric acid.

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It would be the same with the metamorphosis of nitrogen monoxide into nitric oxide—

$$N_2O + O = 2NO,$$

if it could occur. In reality, this reaction does not take place directly, being endothermal. But (pp. 192 and 194) the real existence of the inverse decomposition, which presents an anomaly of the same order and correlative, has been established, viz. a *simple gaseous decomposition effected with contraction:* four volumes being changed into three. The relation is more clearly defined than the first, if not in principle, at least in fact, seeing that it occurs between three gases of which the density is known. If nitric peroxide is the final stage of oxidation of anhydrous nitrogen trioxide by free oxygen, it is not the same with nitrogen trioxide dissolved in water; for dilute solutions of nitrogen trioxide gradually absorb free oxygen, and become gradually changed into nitric acid: $N_2O_3 + H_2O + O_2 = 2HNO_3$ dilute liberates +18·5. If ozone be substituted for oxygen the oxidation of the nitrogen trioxide is instantaneous.

We now return to the action of water on nitrogen trioxide. In presence of water the anhydrous acid becomes wholly or in part hydrated nitrogen trioxide; it also shows a tendency to decompose into nitric acid and nitric oxide. The reaction $3N_2O_3$ gas + water = $2HNO_3$ dilute + 4NO liberates + 4·4. But this last reaction only takes place to any appreciable extent if water be present in sufficient quantity. In this case it is partially decomposed into nitric oxide and oxygen, which gradually transforms another portion of nitrogen trioxide into nitric acid. This may be observed by treating solutions of barium nitrite of various degrees of concentration with dilute sulphuric acid. The immediate reaction here attributed to nascent oxygen is the same as the slow reaction of free oxygen on dissolved nitrogen trioxide.

From the well-known reaction of water on anhydrous nitrogen trioxide, and from experiments on the distribution of baryta among dilute hydrochloric and acetic acid and nitrogen trioxide, the author is of opinion that a double dissociation is observed when nitrogen trioxide is in presence of an insufficient quantity of water, viz. the dissociation of the hydrated nitrogen trioxide, which is partly changed into water and anhydrous acid, and the dissociation of the anhydrous nitrogen trioxide, which is partly changed into oxygen and nitric oxide. The effects are moreover complicated by the ulterior action of the oxygen which disappears in transforming another portion of the nitrogen trioxide into nitric acid.

Under these conditions, the nitric oxide being eliminated as produced, it would seem as if its formation should be indefinitely reproduced.

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But the progressive dilution of the portion of hydrated nitrogen trioxide which remains undecomposed (a dilution resulting from the reaction itself) limits more and more the relative proportion of anhydrous acid up to the point at which the small quantity of nitric oxide remaining dissolved suffices to ensure the stability of the system. Perhaps dilution, carried out to a certain degree, completely arrests the decomposition of the hydrated nitrogen trioxide, no longer permitting any portion of the anhydrous acid to subsist.

In practice it is certain that a final system is realised containing at one and the same time water, dilute nitric acid, and hydrated and diluted nitrogen trioxide. By diminishing the relative proportion of water, the equilibrium would be destroyed; it would also be destroyed by raising the temperature, which gives rise to a liberation of nitric oxide. Conversely, the diminution of water may be compensated for by the lowering of the temperature.

5. *Nitric peroxide.* We shall now examine the degree of stability of nitric peroxide. This body is rightly regarded as the most stable of the oxides of nitrogen; in fact, it may be heated in a sealed glass tube to about 500° for an hour, without showing the least sign of decomposition. It moreover exerts no reaction, either on oxygen in a cold state, or on free nitrogen at a dull red heat under the same conditions. However, under the influence of the electric current the mixture of oxygen and nitric peroxide becomes discoloured, and gives rise to a new compound, *pernitric acid*,[1] about which very little is known.

Nitric peroxide is decomposed into its elements by the electric spark—

$$2NO_2 = N_2 + O_4.$$

After an hour, as much as a quarter was decomposed. After eighteen hours, a mixture was obtained containing in volume—

$$N = 28\,;\ O = 56\,;\ NO_2 = 14.$$

We should note that the decomposition stops at a certain point, as in all cases where the electric spark develops an inverse action. It has, indeed, been known since the time of Cavendish that the spark effects the combination of nitrogen with oxygen. But this combination, effected with dry gases, cannot yield anything but nitric peroxide, seeing that free oxygen always remains, as will now be shown. Operating upon atmospheric air it was found that after an hour 7·5 per cent., that is, a third by volume, had yielded nitric peroxide. Eighteen hours of electric action did not sensibly alter this ratio.

This numerical value is not absolute. An exact measurement would call for more numerous experiments, made under more

[1] "Annales de Chimie et de Physique," 5e série, tom. xxii. p. 439.

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varied conditions, both with regard to electric energy, and pressure and the relative proportions of the gases. The important point is the existence of the limits, as a necessary consequence of the two antagonistic reactions.

The action of water on nitric peroxide deserves attention.

If the water be in small quantity and the nitric peroxide liquid, we obtain, as is well known, at a low temperature, anhydrous nitrogen trioxide—

$$4NO_2 + H_2O = N_2O_3 + 2HNO_3.$$

In the presence of a large quantity of water, nitric peroxide gas, acting gradually, is completely absorbed with the formation of hydrated nitric acid and nitrogen trioxide—

$$4NO_2 + NH_2O = 2HNO_3 \text{ dilute} + N_2O_3 \text{ dilute}.$$

This reaction liberates 7·7 Cal. for $NO_2 = 46$ grms.

But liquid nitric peroxide, in presence of the same quantity of water, gives rise, generally speaking, to some nitric oxide, according to the following reactions, which refer to quantities of substances of which the proportion is variable with the conditions of contact:

$$3NO_2 + nH_2O = 2HNO_3 \text{ dilute} + NO.$$

This reaction, which may be limited almost to nil when contact is gradually effected, liberates, after it takes place, + 4·8 for NO_2.

The following experiment is easy of repetition, and clearly shows both modes of decomposition of nitric peroxide under the influence of water. Into a rather large tube, closed at one end and formed at the other into a funnel, is poured a little liquid nitric peroxide, which, in order to drive out the air, is brought into a state of ebullition, leaving only an insignificant quantity of liquid. The tube is then hermetically sealed. Liquid peroxide is then poured into a similar but much smaller tube; the air is expelled in the same way by boiling, and the tube is closed. After cooling, the large tube, being opened over water, fills completely, owing to the total decomposition of the peroxide into nitrogen trioxide and nitric acid. On the other hand, the small tube is only partly filled, owing to the formation of nitric oxide.

The difference between these two reactions appears to be due to the slight stability of hydrated nitrogen trioxide above defined (p. 197). If the peroxide has at the outset enough water to form hydrated nitrogen trioxide without decomposition the absorption is complete. This is the case with gaseous peroxide and water gradually reacting over a large surface. But if it comes into contact at one point with too small a quantity of water the acid will be partly decomposed with formation of

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nitric oxide which will not be redissolved. Lastly, the contact of the same quantities of substances, effected by degrees, will not give rise to nitric oxide, or if so, only to a very small extent.

6. *Nitric acid.* We have said that anhydrous nitric acid manifests a certain tendency to be spontaneously decomposed at the ordinary temperature, and this appears to be due to the action of light. A few rays of sunlight are sufficient to cause an abundant liberation of oxygen and nitric peroxide. Spontaneous decomposition also takes place in diffused light, but very slowly. This decomposition is accelerated with rise in temperature, without, however, being very rapid up to 43°. It is endothermal, for it absorbs − 2·0; for N_2O_5 gas = $2NO_2 + O$, and is not reversible, dry nitric peroxide not absorbing oxygen at any temperature, as has been proved by exact analysis. It is well known that light also decomposes monohydrated nitric acid.

7. *Heat liberated in the various oxidations effected by nitric acid.* The oxidation of the metals and other oxidisable bodies by nitric acid gives rise, according to circumstances, to the four lower oxides of nitrogen, to nitric peroxide, nitrogen itself, to hydroxylamine, ammonium nitrate, and ammonia, the ultimate term of the reduction of nitric acid by hydrogenated bodies. The following is the method of calculating the heat liberated. Q being the heat supposed to be produced by the union of an equivalent of free oxygen (O = 8 grms.) with the oxidisable body, the latter being changed, further, either into an oxide or soluble salt, we shall have—

The products being	With HNO_3 by	With $HNO_3 + 4HO_2$ ordinary acid.	With HNO_3 dilute.
N_2O_4 gas + O yielded. . .	Q − 9·7	Q − 16·1	Q − 16·9
N_2O_3 gas + O_2 yielded . .	(Q − 9·1) × 2	(Q − 12·3) × 2	(Q − 12·7) × 2
N_2O_3 diss. + O_2 yielded . .	" " "	" "	(Q − 9·3) × 2
N_2O_2 gas + O_3 yielded . .	(Q − 9·6) × 3	" "	(Q − 12·0) × 3
$\frac{1}{2}N_4O_5$ diss. + $O_{2\cdot5}$ yielded .	" " "	" "	(Q − 9·6) × 3·5
N_2O gas + O_4 yielded. . .	(Q − 4·3) × 4	(Q − 5·9) × 4	(Q − 6·1) × 4
N_2 gas + O_5 yielded . . .	(Q − 1·4) × 5	(Q − 2·6) × 5	(Q − 2·8) × 5
$2NH_3O$ diss. + O_4 yielded .	$2H_2O$ in excess.	(Q − 16·3) × 6	(Q − 16·4) × 6
$2NH_3$ + O_3 yielded . . .	" "	(Q − 12·0) × 8	(Q − 12·1) × 8
$2HNO_3NH_3$ diss. + O_8 yielded	{$HNO_3 + H_2O$ in this reaction}	(Q − 10·4) × 8	(Q − 10·5) × 8

It will be seen that the heat liberated constantly increases from nitric peroxide to nitrogen according as the reduction becomes more complete, without, however, attaining to the heat which free oxygen would produce. When hydrogen comes into play, the formation of hydroxylamine and ammonia diminishes, on the other hand, the heat liberated.

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8. We give also the figures relating to nitrogen trioxide.

N_2O_3 dilute =

$N_2O_3 + O$ yielded,	... ...	liberates	$Q - 17{\cdot}4$
$N_2O + O_2$ „	... ...	„	$(Q - 3{\cdot}0) \times 2$
$N_2 + O_3$ „	... ...	„	$(Q + 1{\cdot}4) \times 3$
$N_2H_6O_2 + O_4$ yielded	($3H_2O$ supplemented	„	$(Q - 20{\cdot}1) \times 4$
$2NH_3 + O_6$ „	in the reaction)	„	$(Q - 13{\cdot}0) \times 6$

It is well known that nitrogen trioxide oxidises bodies more easily than nitric acid. This difference is accounted for by the state of dissociation characteristic of nitrogen trioxide (pp. 196 and 197).

The formation of ammonia in oxidations effected at the expense of nitric acid is equally deserving of our attention.

It is a secondary reaction, for it seems to be produced only by the action of free hydrogen (spongy platinum) or by a metal capable of liberating the hydrogen of water by dissolving in more or less diluted acids, which requires the subsidiary relation $Q > 34{\cdot}5$.[1]

In order to form a proper idea of the conditions of this formation, it is well to distinguish the general function of dilute acids, the water in these compounds tending to be destroyed by the metals with liberation of hydrogen, from the special function in virtue of which nitric acid produces ammonia. Take dilute sulphuric or hydrochloric acid in presence of a metal capable of setting free its hydrogen, and a small quantity of nitric acid to intervene, we shall provoke the following reaction :—

HNO_3 dil. $+ 8H = NH_3$ dil. $+ 4H_2O$, which liberates $+ 248{\cdot}2$, or $41{\cdot}4$ Cal. for every equivalent of oxygen (O = 8 grms.) eliminated. The ammonia combining with the excess of sulphuric acid, the heat liberated will be raised by $+ 12{\cdot}4$, which makes altogether for each equivalent of oxygen $+ 43{\cdot}5$.

[1] Or rather $Q > 34{\cdot}5 - S$, S being the heat of solidification of hydrogen, for it would be necessary to compare the metal and hydrogen under the same physical state.

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CHAPTER IV.

HEAT OF FORMATION OF THE NITRATES.

1. THIS chapter will treat of the heat of formation of potassium nitrate and the other nitrates, used in the manufacture of a multitude of explosive mixtures.

The heat of formation of potassium nitrate from its elements is easy to calculate provided we know, at a temperature of about 15°—

(1) The heat of formation of dilute nitric acid from nitrogen and oxygen.

$N_2 + O_5 + H_2O$ + water = $2HNO_3$ dil. liberates + 14·3.

(2) The heat of formation of dilute potash from potassium and oxygen.

$K_2 + O + H_2O$ + water = 2KHO dil. liberates + 82·3.

(3) The heat liberated in the combination of dilute nitric acid and dilute potash.

KHO dil. + HNO_3 dil. = KNO_3 dil. + H_2O liberates + 13·8.

(4) Lastly, the heat which would be liberated if the solid potassium nitrate separated itself from its dilute solution, a heat which is precisely equal in absolute value to the heat absorbed in the act of dissolving the same salt, but with the opposite sign.

KNO_3 dilute = KNO_3 crystallised + water would liberate + 8·3.

The sum of these four quantities, viz.

14·3 + 82·3 + 13·8 + 8·3 = + 118·7 Cal.,

exactly expresses the heat liberated by the union of the elements of crystallised saltpetre, taken at the weight of 101 grms.

$N_2 + O_6 + K_2 = 2KNO_3$ solid liberates + 118·7.

The formation of dissolved saltpetre from the same elements would liberate + 110·4.

From anhydrous potash, nitrogen and oxygen, $N_2 + O_5 + K_2O = 2KNO_3$ solid liberates 70·1.

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From dissolved potash, the formation of dissolved saltpetre, $N_2 + O_6 + K_2O$ dilute $= 2KNO_3$ dilute liberates + 28·1 only.

2. Similarly we have for *sodium nitrate*—

$$N_2 + O_6 + Na_2 = 2NaNO_3 \text{ crystallised} + 110{\cdot}6,$$

and for the dissolved salt + 105·9.

From anhydrous soda, oxygen and nitrogen—

$$N_2 + O_5 + Na_2O = 2NaNO_3 \text{ crystallised} + 60{\cdot}5.$$

From dilute soda the formation of dissolved sodium nitrate liberates + 28·0.

3. The formation of ammonium nitrate—

$$N_2 + O_3 + H_4 = NH_4NO_3 \text{ crystallised} + 87{\cdot}9.$$

The dissolved salt + 81·7.

If we suppose that the equivalent of water necessary to the constitution of the ammoniacal salts is formed beforehand, we have liberated for the salt supposed solid + 53·4 Cal., for the salt supposed dissolved + 47·2 Cal., or + 23·6 Cal. for each equivalent of nitrogen entering into combination, in presence of an excess of water. From ammonia gas and pre-existing water—

$$N_2 + O_5 + 2NH_3 + H_2O = 2NH_4NO_3 \text{ crystallised} + 41{\cdot}2.$$

From dilute ammonia, the dissolved salt + 26·8.

4. The formation of calcium nitrate—

$$N_2 + O_6 + Ca = Ca(NO_3)_2 \text{ anhydrous} + 101{\cdot}3.$$

For the dissolved salt + 103·3.

From anhydrous calcium oxide—

$$N_2 + O_5 + CaO = Ca(NO_3)_2 \text{ anhydrous} + 35{\cdot}3.$$

From dissolved calcium oxide, the salt being likewise dissolved, + 28·2.

5. The formation of strontium nitrate—

$$N_2 + O_6 + Sr = Sr(NO_3)_2 \text{ anhydrous} + 109{\cdot}8.$$

For the dissolved salt + 107·3.

From the anhydrous base—

$$N_2 + O_5 + SrO = Sr(NO_3)_2 \text{ anhydrous} + 41{\cdot}1.$$

From dissolved strontium oxide, the salt being likewise dissolved, + 28·2.

6. The formation of barium nitrate cannot be calculated from the elements, because the heat of oxidation of barium is unknown. Fortunately, this total heat of formation never intervenes in calculations relative to explosive substances. To calculate the thermal effects which barium nitrate produces in combustions it is sufficient to know its heat of formation starting from anhydrous baryta.

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$$N_2 + O_5 + BaO = Ba(NO_3)_2 \text{ liberates } + 47{\cdot}2.$$

From the dissolved base, the salt also being dissolved, + 28·2.

7. It may be remarked that the heat of formation of the alkaline and alkaline-earthy nitrates, by means of gaseous nitrogen, gaseous oxygen, and the dissolved base, is sensibly the same for all. The same figure (+ 28·1) applies equally to magnesium nitrate, as it is formed from solid magnesium hydrate.

8. The formation of the anhydrous nitrates from the anhydrous base and anhydrous nitric acid, whether gaseous or solid, is given in the tables on p. 126. Similarly, the formation of the solid nitrates, formed by solid hydrated nitric acid and basic hydrates also solid, is given in the table on p. 127.

9. We should further note that the metamorphosis of the alkaline nitrites into nitrates $M(NO_2)_2$ dissolved + O_2 = $M(NO_3)_2$ dissolved, liberates a quantity of heat nearly equal to + 21·7, and sensibly the same whatever be the base of the salt (p. 178).

10. The heat of formation of the anhydrous magnesium, iron, cobalt, nickel, and manganese nitrates, cannot be calculated, these salts being only known in the hydrated state. In the dissolved state we have, from the metals and the metallic oxides—

$N_2 + O_6 + Mg$	liberates	103·0	$N_2 + O_5 + MgO$	liberates	+ 58·1
$N_2 + O_6 + Mn$	,,	73·5	$N_2 + O_5 + MnO$	,,	+ 26·1
$N_2 + O_6 + Fe$	,,	59·5	$N_2 + O_5 + FeO$	,,	+ 25·0
$N_2 + O_6 + Zn$	,,	67·3	$N_2 + O_5 + ZnO$	,,	+ 24·1
$N_2 + O_6 + Co$	,,	56·9	$N_2 + O_5 + CoO$	,,	+ 24·9
$N_2 + O_6 + Ni$	,,	56·3	$N_2 + O_5 + NiO$	,,	+ 25·6
$N_2 + O_6 + Cd$	,,	57·6	$N_2 + O_5 + CdO$	,,	+ 24·4
$N_2 + O_6 + Cu$	,,	39·8	$N_2 + O_5 + CuO$	,,	+ 21·8

11. The formation of lead nitrate from the elements

$$N_2 + O_6 + Pb = Pb(NO_3)_2 \text{ anhydrous liberates } + 52{\cdot}8.$$

That of the dissolved salt + 48·7.

The formation of the same salt from the anhydrous oxide,

$$N_2 + O_5 + PbO = Pb(NO_3)_2, \text{ liberates } + 27{\cdot}3.$$

The dissolved salt + 23·2.

The formation of silver nitrate from the elements

$$N_2 + O_6 + Ag_2 = 2AgNO_3 \text{ anhydrous liberates } + 28{\cdot}7.$$

That of the dissolved salt + 23·0.

The formation of the same salt from the oxide,

$$N_2 + O_5 + Ag_2O = 2AgNO_3, + 25{\cdot}2.$$

The dissolved salt + 19·5.

12. We will add the following general remarks. Between the formation of two salts obtained by the union of the

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same alkaline base with two distinct acids, these salts being considered under the solid and anhydrous form, we find a nearly constant thermal difference, whatever be the base, when we reckon the quantities of heat liberated from the elements up to the anhydrous salts. For example, the formation of the anhydrous potassium, sodium, ammonia, calcium, strontium, lead and silver sulphates, liberates a mean value of 54 Cal. more than the formation of the corresponding nitrates.

A similar difference exists between the nitrates and the majority of the oxygen salts. It exists even between the alkaline chlorides, bromides, and iodides, without, however, extending itself to the anhydrous metallic chlorides.

13. These numbers permit, as will be shown later, of estimating the heat liberated by any decomposition or definite combustion of service powder or other powders, inflammable materials or explosive mixtures constituted by the nitrates. It is with the aid of analogous data, derived from the heat of formation of nitric acid, that we can calculate the heat of formation of nitroglycerin, and of organic compounds derived from nitric acid. The figures thus calculated agree moreover with the experiments of Sarrau and Vieille, as far as can be expected in verifications of this nature.

14. If this agreement is dwelt upon, it is because, in the author's opinion, the applications of explosive substances, as well as the applications of human industry, need to be guided by theoretical notions. We must raise ourselves above empiricism if we wish to obtain the most favourable results. It is thus that blasting powder, so long exclusively employed in practical applications, tends to-day to be replaced by dynamite in the majority of its uses. Now this substitution is encouraged and regulated by theory. Indeed, the latter teaches us that blasting powder, as well as service powder, is far from utilising in the best manner the combustive energy of nitric acid.

In the combustion of ordinary powder, the products formed are neither the most oxidised, nor those which would liberate the most heat for a suitable proportion of the various ingredients, seeing that the maximum of heat which would be developed by a known weight of saltpetre acting on the sulphur and the carbon does not correspond to the maximum volume of the gases liberated. Between these two data of the problem, empiricism has led to a sort of compromise being adopted, which is our traditional powder. But it would be far preferable to arrange in such a manner that the maximum of the two effects should occur in it for the same proportions.

This is not all. The formation of potassium nitrate itself, reckoned starting either from nitric acid or the elements, corresponds to very powerful affinities and gives rise to a greater liberation of heat, and consequently to a greater expenditure of

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energy than most of the other combinations derived from nitric acid.

Theory therefore shows that saltpetre is not a favourable agent of combustion; and in this way it explains the superiority of the organic compounds derived from nitric acid, and especially the nitric ethers, such as nitroglycerin. As a matter of fact, the author's experiments show a much inferior liberation of heat, that is to say, a greater preservation of energy in the formation of these substances. The energy introduced into an explosive compound, formed by the same weight of nitric acid, is in nitroglycerin double that which is found in service powder. Hence it is easy to understand how the abandonment of blasting powder for industrial purposes is gradually extending. Perhaps it will be soon the same with service powder, if practice, guided by the new theories, succeeds in discovering more active nitrogenated compounds than powder, which will satisfy the manifold conditions called for in the use of explosive substances in firearms.

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CHAPTER V.

ORIGIN OF THE NITRATES.

§ 1. Natural Nitrification.

1. The formation of nitre in nature has long been regarded as a most obscure phenomenon.

It has long been known that the alkalis and the alkaline carbonates, when exposed for some time to the air, yield the reactions of nitric acid. Stahl had already observed this two hundred years ago. At all times and in all places, under the action of natural forces, there are produced small quantities of nitrates.

2. There also exist certain plants which appear to produce saltpetre, at the expense of the nitrated combinations contained in the soil or in manures. Such are borage, pellitory, beetroot, tobacco, and especially plants of the family of the amarantaceæ.[1] Nevertheless, the conditions of natural nitrification are still imperfectly known.

3. It is not proposed to refer here to the sodium nitrate mines in Chili, formed under the influence of geological conditions with which we are unacquainted, but only to the nitrification going on every day under our eyes.

4. In the first place, we know that nitric acid is formed in the atmosphere in small quantities under the influence of storms, simultaneously with a little ammonium nitrate, and introduced into the soil by rain and there united to the bases. This formation is of great interest. But a searching examination has shown that such an origin does not suffice to account for the production of the nitrates in nature and their concentration in a soil impregnated with animal matter.

5. As a matter of fact natural nitrification results principally from the slow oxidation of the nitrogenous organic compounds, or even of ammonia, effected by the oxygen of the air, with the aid of water and of an alkaline or earthy carbonate.

[1] Compare note sur l'attraction du salpêtre, par Faucher ("Mémorial des poudres et salpêtres," p. 162. 1883).

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Too strong a light checks it. Clayey substances and porous matters appear to favour it, but it does not appear that free nitrogen intervenes in this mode of formation of saltpetre.

6. Various questions here present themselves. Thus it has been asked whether this slow oxidation is simply provoked by the presence of clay and porous bodies, as occurs in Kuhlmann's experiments, where the ammonia is changed into nitrous vapour and nitric acid on contact with spongy platinum and oxygen at about 300°.

Are the humus principles, the sulphuretted and ferruginous compounds, and the other oxidisable bodies which are decomposed in the soil, at the same time that nitre is formed, the medium of some special reaction?

Do they provoke the oxidation of the ammonia, becoming oxidised themselves, as occurs with copper in presence of the air? Phosphorus does in fact exert an analogous reaction, and this influence has also been attributed to humus.

Does an oxidising body properly so called intervene, after the manner of potassium bichromate and sulphuric acid, or of manganese dioxide at a red heat, when the latter agent changes the ammonia into nitrous vapour?

Does ozone play some such part, as held by Schönbein, according to whom certain plants emit ozone, a substance, in fact, capable of oxidising ammonia at ordinary temperatures, with formation of nitrite.

Lastly, do the mycoderms and microbes cause this oxidation after the manner of a fermentation?

Such are the principal hypotheses which have been brought forward since the eighteenth century up to our time to explain the apparently spontaneous formation of nitre in nature.

At the present day these questions, which have been for so long a time the object of controversy, appear to have made a decisive step forward in consequence of the recent experiments of Schloesing and Müntz.[1]

7. These investigators have found that the nitrification of ammonia and the nitrogenous organic compounds takes place under the influence of pointed, rounded, or slightly elongated organised corpuscles, sometimes adhering in pairs of very small dimensions, and very similar in appearance to the corpuscular germs of bacteria. These corpuscles occur in all arable soils and in sewage water, which they aid in purifying. They cause the fixation of oxygen upon ammonia and nitrogenous substances, generally forming nitrates, sometimes nitrites, when the temperature is below 20° or the aeration insufficient. The nitrites also result from the reduction of the original nitrates

[1] "Comptes rendus," tom. lxxxiv. p. 301, 1877; tom. lxxxv. p. 1018; tom. lxxxvi. p. 892; tom. lxxxix. pp. 891 and 1074: 1879.

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by the intervention of the butyric ferment and of analogous secondary ferments.[1]

Their action is exerted between determinate limits of temperature. Below 5° it is inappreciable, becoming appreciable at 12°. It becomes more and more active as the temperature rises to about 37°, at which temperature the nitrification is ten times more rapid than at 14°, though still rather slow, all the other conditions moreover being the same. Beyond this it grows slower; at about 45° it is less active than at 15°, and ceases completely at 55°.

According as the temperature rises, and especially if it be brought to 100°, the vitality of the corpuscles diminishes, so that mould or water in course of nitrification loses this property without recovering it after cooling. They also perish under the influence of the vapours of chloroform and antiseptics.

Moisture is indispensable to them. It is even sufficient to dry in the air a fertile piece of mould for it to become sterile after a time. The corpuscles do not support a prolonged privation of oxygen, at least when operated upon in a liquid.

They act equally well in the dark or under the influence of a moderate light, but a strong light is prejudicial to them.

Their action requires the aid of a slight alkalinity, due either to the presence of calcium carbonate, or to that of two to three thousandth parts of alkaline carbonates. Beyond this degree alkalinity injures them, which accounts for the unfavourable influence exerted by liming upon nitrification. The development of the nitric ferment in water requires the simultaneous presence of an organic substance and a nitrogenous compound. But the ratio between the carbonic acid and the nitric acid produced is in no way constant. It is the same with the absorption of oxygen, which is continually going on at the expense of a soil which has been rendered sterile by a temperature of 100° or by the action of chloroform vapours.

The nitric ferment is multiplied by sowing a nourishing liquid, or earth, with a small piece of arable soil or a few cub. cms. of sewage. It does not generally exist in the dust in the air. Its multiplication is slow, and seems to be effected by budding. The existence or absence of porous bodies appears to have very little to do with nitrification, contrary to the views formerly held.

Ordinary mould and mycoderms are quite distinct from this ferment, and even contrary to its action. In fact, they destroy

[1] Dehe rainet Maquenne, "Comptes rendus," tom. xcv. p. 691; Gayen, same collection, tom. xcv. p. 1365. These auxiliary ferments, or rather perturbators, reduce inversely the nitrates with production of nitrites, nitrogen monoxide, free oxygen, and even of ammonia, according to their nature and the greater or less intensity of their action. The hyponitrites must also intervene.

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the nitrites, and change them into organic nitrogenous compounds during the development of their mycelium. They act in the same way upon ammonia or the ammoniacal salts, and even by preference. Later on, during fructification, a portion even of the nitrogen is eliminated in the gaseous form, sometimes with intermediate reproduction of ammonia.

These observations, as a whole, show the existence of particular organised beings, analogous to the acetic ferment, which cause the fixation of oxygen upon ammonia and nitrogenous organic compounds, and consequently the change of these substances into nitrates. They go far to resolve the problem of nitrification, effected in nature at the expense of the nitrogenous or ammoniacal compounds; a problem, moreover, which is quite distinct from the fixation of free nitrogen taken from the atmosphere. It is, however, allied to it; for natural nitrification is effected upon already formed and pre-existing nitrogenous compounds.

§ 2. Chemical and Thermal Conditions of Nitrification.

1. These facts being admitted, it will be useful to show that the study of the quantities of heat liberated during the act of natural nitrification throw a fresh light upon the latter. In order to render the discussion clearer, it will be best to attempt at the outset to define the chemical conditions of this oxidation, as far as can be done in the present state of our knowledge.

2. The most developed experiments which have been performed on the chemical conditions of nitrification are, even at the present day, those of Thouvenel, although they date from nearly a century ago.[1] They show that nitrification takes place principally in connection with the gaseous compounds produced in putrefaction, mixed with an excess of atmospheric air. We know at the present day that the most important of these compounds are ammonia, ammonium carbonate, hydrosulphide, hydrocyanide, and perhaps hydrocyanic acid. That it requires the aid of moisture. That it is more easily effected in the presence of the alkaline or earthy salts than in their absence. Lastly, it hardly occurs save with carbonates, to the exclusion of sulphates. For example, a basket pierced with holes, and containing well-washed chalk, being placed over blood in a state of putrefaction, the chalk was found after some months to contain 2·5 per cent. of nitrate. A plate, containing washed mortar and placed in the atmosphere of a stable, contains nitrates at the end of three weeks, etc. These conditions agree with the biological conditions which preside at the

[1] "Mémoires de l'Académie des Sciences" (Savants étrangers), tom. xi. 1787.

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development of the nitric ferment, as they have been defined above.

3. These various circumstances may also be accounted for from the chemical point of view. We proceed to enter into detail upon this subject. Ammonia and oxygen are, we have said, the generators of the nitrates. Take, first, ammonia. The liberation of gaseous ammonia, supplied by the slow transformation of nitrogenous organic principles, takes place only in an alkaline medium. In an acid liquid it is clear that this liberation cannot take place.

Neither can it take place in a liquor capable of forming only neutral and fixed ammoniacal salts by double decomposition, such as the sulphate.

On the other hand, it is facilitated when the liquor can give rise by double decomposition to a volatile and partly dissociated ammoniacal salt,[1] such as the carbonate. The presence of a fixed alkali, or of an alkaline carbonate, is not only useful for setting free the pre-existing ammonia of the ammoniacal salts; it further causes the generation of ammonia, at the expense of the principal organic nitrates, in virtue of a sort of predisposing affinity, owing to the intervention of the excess of energy resulting from the saturation of the bases by the acids produced during oxidation. Let us now turn to the latter phenomenon.

Air, or rather its oxygen, is indispensable, because we are here dealing with a phenomenon of oxidation incapable of taking place in a reducing medium, such as a substance undergoing putrefaction.

From the same point of view, the presence of an alkali, or of a salt having an alkaline reaction, is very efficacious in accelerating the oxidation of organic principles by the oxygen of the air, and at the ordinary temperature, while they offer much more resistance in an acid medium. The mode itself in which the oxidation of ammonia takes place during nitrification helps to account for the efficacy of the fixed alkalies and their carbonates. Now, the slow oxidation of ammonia develops nitrous, then nitric acid, which must gradually combine with the portions of free and non-oxidised ammonia. Hence, finally, results ammonium nitrate, that is, a salt fixed at the ordinary temperature and devoid of alkaline reaction. If a nitrogenous principle, taken by itself, were operated upon, half the ammonia would thus be withdrawn from the oxidising action, and at the same time the liquor would constantly tend to lose the alkaline reaction due to the existence of free ammonia, a reaction which facilitates oxidation. But the alkaline carbonate retains the alkaline character, because it gradually transforms the nitrate of ammonia into fixed alkaline nitrate and ammonium carbonate,

[1] "Essai de Mécanique Chimique," tom. ii. p. 717.

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which is partly dissociated, with formation of free ammonia. Now the latter is capable of ulterior oxidation.

Further, the author has established, by direct and accurate experiments, that dissolved ammonium nitrate in presence of potassium or sodium carbonate is instantly transformed into potassium or sodium nitrate and ammonium carbonate, the strong acid taking by preference the strong base and leaving to the weak acid the weak base.[1] Calcium carbonate produces the same reaction. We shall return to the consideration of this reaction on account of the part which it plays in natural nitrification.

If we now consider the thermal phenomena which accompany these various chemical reactions, we shall be able to understand more fully the part played by them in nitrification.

4. Take first the transformation of ammonia into nitrous acid, nitric acid, and ammonium nitrate[2]—

Nitrous acid, $NH_3 + O_3 = HNO_2 + H_2O$.
Nitric acid, $NH_3 + O_4 = HNO_3 + H_2O$.
Nitrate ammonium, $2NH_3 + O_4 = NH_4NO_3 + H_2O$.

The formation of gaseous ammonia by its elements

$$N + H_3 = NH_3$$

liberates, according to the author's measurements, + 12·2 Cal.; that of dissolved ammonia liberates + 21·06 Cal.

Lastly, the formation of water,

$$H_2 + O = H_2O,$$

liberates + 34·5 or + 29·5 according as the water is produced in the liquid or the gaseous state. It follows from the above that the oxidation of ammonia, whether rapid or slow, liberates the following quantities of heat according to the nature and the state of the products to which it gives rise.

(1) *Formation of nitrogen.*

$$2NH_3 + O_3 = N + 3H_2O.$$

Gaseous ammonia and gaseous water + 88·5 - 12·2 = + 76·3.
Dissolved ammonia and liquid water + 103·5 - 21·0 = + 82·5.
Gaseous ammonia and liquid water + 103·5 - 12·2 = + 91·3.

(2) *Formation of nitrous acid.*

$$NH_3 + O_3 = HNO_2 + H_2O.$$

Gaseous ammonia, water, and dilute nitrous acid ... + 87·1.
Dissolved ammonia, water, and dilute nitrous acid ... + 78·3.

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[1] "Essai de Mécanique Chimique," tom. ii. p. 717.

[2] It would be well, no doubt, also to establish analogous calculations for the hyponitrites (see p. 188).

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(3) *Formation of nitric acid.*

$$NH_3 + O_4 = HNO_3 + H_2O.$$

Gaseous ammonia, water, and gaseous nitric acid + 81·2.
Gaseous ammonia, liquid water, dilute nitric acid + 105·6.
Dissolved ammonia, dilute nitric acid .. + 96·8.

(4) *Formation of dissolved ammonium nitrate.*

$$2NH_3 + O_4 = NH_4NO_3 + H_2O.$$

Gaseous ammonia, dissolved nitrate ... + 125·3.

Or, for $NH_3 + O_2$, + 62·6.

(5) *Transformation of dissolved ammonium nitrite into nitrate by fixation of oxygen.*

This transformation, and more generally that of a dissolved nitrite into a nitrate of the same base, liberates + 21·8; a value which is sensibly the same for the various dissolved alkaline nitrites. This value offers the more interest, as the change of the nitrites into nitrate and the inverse transformation take place in nature, as shown by the very curious experiments of Chabrier[1] and the recent researches of Gayon, Deherain, and Maquenne.

The presence of the nitrites has been remarked in stables, as co-existing with the nitrates, by Goppelsröder. They also exist in rainstorms. The hyponitrites should also be searched for.

5. All the foregoing figures are applicable to the oxidation of ammonia by free oxygen, whether this oxidation take place by sudden combustion, or whether it be excited at a lower temperature by spongy platinum, or whether it take place slowly and in the cold state, as in nitrification.

They show that the formation of the oxygenated compounds of nitrogen by the oxidation of ammonia always takes place with liberation of heat. It can, therefore, always take place without the aid of any foreign energy; the microbes confining themselves, as in all cases where their action is exerted, to cause a formation, to which they contribute no energy of their own.

Conversely, the formation of ammonia by the action of hydrogen on the various oxides of nitrogen liberates more heat than the same formation effected by means of free nitrogen; which accounts for the greater facility of the first reaction. But it is not necessary to go at length into this subject, which is foreign to the question of nitrification, though it plays a certain part in the reduction of the nitrates to the state of ammonia by natural agents.

6. Various experiments have been made with a view to discovering whether free ammonia could be directly oxidised by

[1] "Comptes rendus des séances de l'Académie des Sciences," 1871.

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the oxygen of the air, at the ordinary temperature, with the aid of time, and without that of the microbes.

Large flasks full of air, well closed, and exposed to a moderate light in presence of potash and its dissolved carbonate, were employed. There was also introduced simultaneously with the alkalies a small quantity of oxidisable substances, naturally indicated for the purpose, such as glucose, and essence of turpentine. But no nitre was obtained even after several months (March to June, 1871). In spite of these negative trials, the oxidation of ammonia during nitrification cannot be questioned, but the conditions attendant upon it are only known since the already cited experiments of Schloesing and Müntz.

7. It will be interesting to further examine the integral transformation of ammonium nitrate into potassium nitrate. It has been stated, in fact, that ammonia could yield at first, in becoming oxidised, ammonium nitrate. It can further be shown that the whole of the nitrogen contained in this salt passes to the state of potassium nitrate.

Two phases manifest themselves during this change.

The first transformation produces potassium nitrate and ammonia, finally oxidisable. This transformation is effected, both in nature and in the laboratory, by dissolved potassium carbonate. The double decomposition between the two salts, separately dissolved in equivalent proportions, gives rise, according to the author's experiments, to a noteworthy thermal phenomenon; that is, to an absorption of 3 Calories per equivalent. This phenomenon shows that the potassium carbonate is changed into ammonium carbonate in the liquor; since the formation of the latter salt by means of the dissolved acid and the dissolved base, liberates far less heat than that of the potassium carbonate.[1]

Now the ammonium carbonate thus formed in the solution disappears by reason of the evaporation of the liquor, or even by the mere fact of the diffusion of carbonic acid and ammonia into the atmosphere; so that there remains nothing at the end but potassium nitrate, either in the liquor concentrated by evaporation, or in the efflorescent residuum which this liquor yields by spontaneous evaporation.

The ammonia, on the other hand, after having been brought to the gaseous state, is separated from the carbonic acid, owing to the diffusion of the two gases into the atmosphere; it is oxidised afresh under the influence of the same causes, whichever they may be, that have already changed the half of this base into nitric acid. The other half becomes in its turn ammonium nitrate, and the latter body again reproduces ammonia by the same mechanism, but it does not reproduce more than a quarter

[1] "Essai de Mécanique Chimique," tom. ii. p. 717.

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of the original quantity. The sequence of reactions goes on in this way and the whole of the ammonia is finally changed into potassium nitrate, provided the liquor contains an excess of potash.

The transformation of ammonium nitrate into calcium or magnesium nitrates takes place in virtue of similar reactions, with this difference, however, that the double decompositions can take place between ammonium nitrate and the earthy carbonates, especially when the latter are dissolved by carbonic acid (bicarbonates). Magnesium carbonate can also be dissolved in another way, forming a double salt with ammonium carbonate. Notwithstanding these diversities of detail, the general mechanisms remain the same whether in the case of potassium, calcium, or magnesium nitrates.

8. Let us now refer nitrification to gaseous ammonia, and dissolved potassium nitrate, without concerning ourselves with the media, and calculate the heat liberated.

$2NH_3$ gas + $4O_2$ + K_2CO_3 dilute = $2KNO_3$ dilute + $3H_2O$ + CO_2 dissolved. This reaction liberates 109·2, and hardly differs from the formation of dilute nitric acid.

9. In cases where nitrification is not effected at the expense of free nitrogen and oxygen, but at the expense of free oxygen and of a pre-existing nitrogenous compound, such as ammonia, the cyanides, etc., the heat liberated varies with the nature of the said compound; but it is almost independent of the particular nature of the dissolved alkali which takes part in the reaction (potash, soda, lime); it is also the same with the various carbonates compared with one another. This results from an observed fact, viz. that the union of the same acid with the various fixed alkalis liberates nearly the same quantities of heat.

It will be seen from these data that natural nitrification once excited and under the conditions in which it occurs, that is, in presence of alkaline or earthy carbonates, can be effected without the aid of any foreign energy.

10. It is effected all the easier, however, when this aid is not wanting, seeing that the oxidation of the nitrated or non-nitrated organic principle is developed at the same time as that of the ammonia yielded by those principles, and liberates an additional quantity of heat. This point deserves to be developed.

The presence of an alkali, free or carbonated, facilitates, as has been said, the absorption of oxygen by the organic principle. Here is another fact which may be accounted for by thermal considerations; for the oxygen of the said principles forms acids, the formation and the simultaneous combination of which with the alkali liberate more heat than the pure and simple formation of the same free acid would do. For example, the

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change of alcohol into potassium acetate, when in contact with dilute potash, liberates 13 Calories more than its change into free acetic acid.

The oxidation itself often becomes more thorough under the influence of this additional work, which further increases the liberation of heat. This is the case with alcohol. It is well known how difficult it is to oxidise alcohol by free oxygen at a low temperature and without a medium. It is necessary to raise the alcohol, taken by itself, to a very high temperature in order to cause it to absorb oxygen, forming at first aldehyde and acetic acid. But it is otherwise if alcohol be placed in presence of oxygen and of an alkali simultaneously; then the alcohol is gradually oxidised at the ordinary temperature, and it forms not only acetic acid, but even oxalic acid, or rather an oxalate. Now the transformation of alcohol into dissolved potassium oxalate liberates a quantity of heat (288) nearly double that produced by the transformation of alcohol into acetate (136).

Phenomena of the same kind are very common in organic chemistry. They certainly play a part in natural nitrification. In the author's opinion their interpretation should be sought in thermo-chemical considerations, seeing that chemical reactions are the easier, *cæteris paribus*, the greater the amount of heat liberated by them.

11. We shall show, lastly, how an analogous concurrence may be brought about, under the hypothesis that the nitrates result directly from the oxidation of nitrogenous organic principles. It will be sufficient, to take an exact instance, to calculate approximately the heat liberated in the nitrification of hydrocyanic acid, or rather of potassium cyanide, a calculation not without interest in itself, the cyanides often existing in bricks and other materials capable of nitrification. Take, therefore,

$$CNK \text{ dissolved} + 5O = KNO_3 + CO_2 \text{ gas.}$$

The heat liberated amounts to + 177 Cal. It is nearly double the heat liberated in the nitrification of ammonia, at the expense of dissolved potassium carbonate. This excess is due in a great measure to the oxidation of the carbon; it is probably to be met with in the oxidation of the other nitrogenous organic substances. Gaseous hydrocyanic acid and dilute potash would liberate + 186 Cal. in yielding an equivalent of potassium nitrate.

Lastly, dissolved ammonium cyanide and potash absorb nine equivalents of oxygen in being transformed into potassium nitrate—

$$CNH.NH_3 \text{ dilute} + K_2O \text{ dilute} + 9O = 2KNO_3 \text{ dilute} + CO_2 \text{ gas} + 2H_2O,$$

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and liberate + 279·1 Cal.; + 139·5 Cal. per equivalent of nitrogen.

All these numbers exceed that corresponding to the oxidation of ammonia alone (+ 109), there is therefore ground for supposing that nitrification is facilitated by the simultaneous oxidation of the carbon contained in the organic principle.

§ 3. On the Transformation of Free Nitrogen into Nitrogenous Compounds.

First Section.—Problem of the Fixation of Nitrogen in Nature.

1. The problem of the fixation of the nitrogen of the air and its transformation into nitrogenous compounds, such as the nitrates or ammoniacal salts in the mineral kingdom, the alkalis, amides, and albumenoid compounds in the vegetable and animal kingdom, has long formed a subject of controversy. A nitrogenous compound of any class being formed, it is easier afterwards to change it into a compound of another class, and it is precisely of this transformation that we have been treating in the foregoing paragraphs. But there still remains the problem of the formation of this initial compound, for nitrogen does not combine directly with any body at the ordinary temperature and in the absence of the conditions which will presently be indicated. On the other hand, the natural nitrogenous compounds tend constantly to be destroyed, under the diverse influences of slow or rapid combustion, fermentation, putrefaction, and even of the normal nutrition of animals, influences which all tend to set free nitrogen. Hence it follows that natural nitrogenous compounds being constantly destroyed and never reproduced, the actual supply of them should continually diminish. Thus it is that the methodical researches made on the use of manures in agriculture have not done much more than reveal causes of destruction, without establishing with certainty any general cause of regeneration, that is to say, any cause sufficiently powerful to explain the reproduction of the nitrogenous compounds. Nevertheless, vegetation is indefinitely prolonged, and without languishing, on the same spot of ground, whenever it is not over stimulated and rendered exhaustive by human industry, a fact which seems to show that there exist slowly acting causes of reproduction of nitrogenous compounds, sufficiently efficacious to support spontaneous vegetation. It is these causes which we are about to consider.

2. *Slow oxidations.* From the purely chemical point of view, and under natural conditions, free nitrogen may be united to oxygen in certain slow oxidations. It is beyond question, for instance, that air kept for some time in contact with phosphorus contains several thousandth parts of oxynitric compounds, it being sufficient to agitate this air with lime or baryta water, and

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to evaporate the latter to obtain small quantities of nitrates. Even in sudden oxidations, hydrogen, and the hydrocarbon gases, burning in oxygen mixed with nitrogen, yield some traces of the oxygen compounds of nitrogen.

3. *Ozone.* Schönbein attributed the first formation to the action of ozone, formed by phosphorus, on free nitrogen. Ozone, he said, oxidises nitrogen in the cold, especially in presence of water or alkalis; its formation in the atmosphere would account for the natural formation of nitric acid, which would reduce the problem of the formation of the latter to that of ozone.

But this theory has fallen in face of the experiments separately by Carius and the author,[1] experiments from which it results that pure ozone does not oxidise nitrogen in any way. The assertions of Schönbein, according to which the evaporation of water in presence of nitrogen is sufficient to cause the combination of these two bodies and the formation of ammonium nitrate, have likewise been found erroneous, since he seems to have neglected the pre-existence of traces of nitrates in the waters upon which he operated.

It is none the less certain that the slow oxidation of phosphorus and the rapid combustion of hydrogen and the hydrocarbon bodies develop nitrous compounds. But these are exceptional reactions not sufficiently widespread nor efficacious to account for the whole of the natural phenomena.

4. *Function of porous bodies.* The same may be said of Longchamp's theory, according to which nitrogen is absorbed in presence of alkalis and porous bodies. The sole experiments which have been cited in confirmation up to the present, are those of M. Cloez, according to which a million litres of air, directed during a period of time amounting to six months across pumice-stone impregnated with potassium carbonate, yielded a few milligrammes of nitrates. This quantity is too small for its origin to be attributed with certainty to free nitrogen. The least trace of nitrated compounds of mineral or organic origin, not arrested by the purifying agents (acid and alkaline) in passing across, perhaps even a trace of neutral and volatile compounds, would be sufficient to account for such small quantities of nitrates. Whatever be the interest of these observations, there is therefore no certain conclusion to be derived from them, so long as the conditions involve the formation of traces of nitrates only.

5. *Nascent hydrogen.* It has, in like manner, been supposed that free nitrogen can be united to hydrogen, especially under the conditions in which the latter is formed at the expense of hydrogenated bodies. The formation of rust by the slow oxidation of iron is especially cited with reference to this point. In this formation traces of ammonia have been found. But these

[1] "Annales de Chimie et de Physique," 5e série, tom. xii. p. 440.

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traces are attributed by the majority of authors to the presence of nitric acid[1] or other nitrogenous compounds in the atmosphere. The appearance of ammonia in the reaction of the metals (iron, zinc, arsenic, lead, tin) upon dissolved alkaline hydrates, appears in the same way due to the existence of a trace of cyanides or nitrates in these alkalis.

6. *Earthy substances.* Mulder has asserted that during the slow alteration of earthy substances, small quantities of ammonia are formed. But quantitative measurements have not shown that these quantities are capable of compensating the incessant loss of nitrogen produced during vegetation.

7. Hence the purely chemical reactions which take place in nature seem insufficient to explain the incessant reproduction of the nitrogenous combinations.

Nevertheless, the latter does take place, but it results, in the opinion of the author, from an energy foreign to purely chemical actions.

It is electricity which causes the fixation of free nitrogen, and principally at the ordinary temperature and at the low tensions which electricity possesses at the surface of the earth everywhere and at all times, even during the finest weather.

Second Section.—Actions of Electricity in general.

1. Electricity can be employed under various forms to excite chemical reactions, viz. voltaic current, electric arc, electric spark, or silent discharge. The last-named mode of action may itself be effected in several ways; for instance, by suddenly varying the potential, by the effect of rapid discharges, sometimes all in one direction, sometimes in alternate directions, or again by maintaining the potential constant throughout the whole duration of the experiment. Now it is certain, and this is a fundamental fact, that all the modes of action of electricity, with the exception perhaps of the voltaic current traversing liquid electrolytes, bring about the chemical activity of nitrogen, but in very different ways. Before reviewing them, let us decide a preliminary question.

2. Does there exist a special isomeric modification of nitrogen analogous to ozone, which is the origin of the nitrated compounds? This is the point which the author has set himself to clear up. He has observed that the activity of nitrogen is only called into play at the moment when this element is submitted to the action of electricity. Pure nitrogen, however, does not undergo appreciable permanent modifications either by the action of the arc, or by that of the spark, or of the silent discharge. In fact, nitrogen brought into immediate contact with hydrogen at a distance of a few centimetres, by silent discharge tubes, or by spaces in which it undergoes the action

[1] Cloez, "Comptes rendus," tom. lii. p. 527.

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of the arc or that of a series of strong sparks, never shows any sign of combination. It is the same with nitrogen brought afterwards into contact with oxygen, and also with organic substances. In all known cases it is necessary that nitrogen and the organic substance, or hydrogen, or oxygen should simultaneously undergo the electric action for the combination to take place.

3. The appliances in which the arc or spark is first caused to act on nitrogen can be easily imagined.

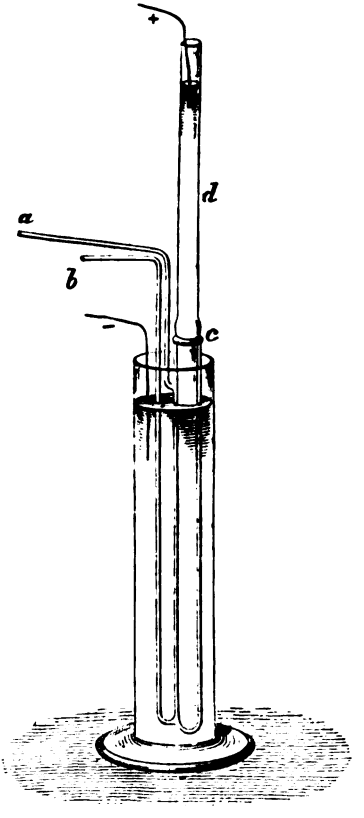

Fig. 31.—Berthelot's silent discharge apparatus for the modification of gases.

For the silent discharge the apparatus shown in the annexed figure is employed.

The apparatus consists of a glass tube, *c*, provided with two tubular passages, *a* and *b*. Another tube, *d*, penetrates into the first tube which surrounds it, and is ground into it at *c*. It is filled with a conducting liquid (water acidulated with sulphuric acid), the whole being placed in a test glass filled with the same liquid.

The electrodes of a powerful Ruhmkorff machine communicate with the liquid in the internal tube and with the external liquid.

The silent discharge takes place in the annular space comprised between the tubes *c* and *d*. It acts upon the gases which enter at *a* and escape at *b*. The nitrogen which issues from this apparatus has acquired no fresh property.

4. The same negative results were obtained by the author with hydrogen in presence of organic substances, either nitrogen or oxygen, immediately after the hydrogen had undergone the action of the sparks, or of the silent discharge, results which are very different from those observed with oxygen. There does not therefore appear to exist for nitrogen or hydrogen any permanent electrical modification, analogous to that of oxygen forming ozone.

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Third Section.—Action of the Voltaic Arc and the Electric Spark.

1. We shall now study the action of electricity under its various forms in bringing about nitrogenous combinations, by acting upon nitrogen in presence of the other elements.

Under the form of the voltaic arc, or the spark, electricity produces in fact the union of nitrogen with oxygen (synthesis of the nitric compounds), the union of nitrogen with hydrogen (synthesis of ammonia), the union of nitrogen with acetylene (synthesis of hydrocyanic acid).

2. These reactions can easily be produced with the following apparatus, which does not require either the use of platinum wires fused into the glass or special conductors. Bent glass tubes and free platinum wires suffice.

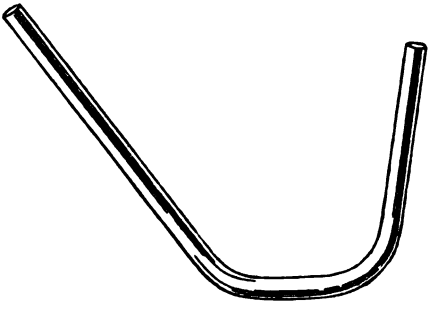

Fig. 32.

The following is the arrangement. The gas (measured or not) is placed in an ordinary test-tube, in a mercury trough; then into this test-tube are introduced two gas-tubes, twice bent to slightly obtuse angles (Fig. 32), but still keeping the same direction. The tubes being open at both ends, their introduction is effected without difficulty and without establishing communications with the atmosphere. This done, a thick and long platinum wire is taken, of which the length considerably exceeds that of the bent tube, and it is introduced by the external orifice of one of the tubes, by pushing it gently through the mercury which fills the tube; it is thus got past the bends until its end passes out of the internal orifice of the tube. The same operation is performed with a second platinum wire slipped through the second tube.

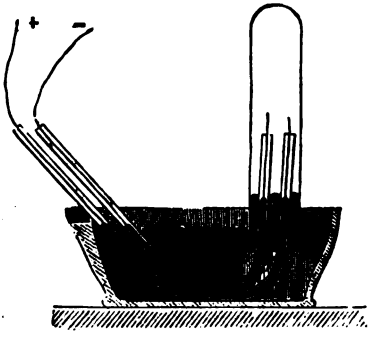

Fig. 33.—Action of the electric spark on gases.

Two insulated conductors are thus obtained, which are put into communication with the two poles of a Ruhmkorff coil, or any other generator of high tension electricity. The spark passes between the two points situated in the interior of the test-tube, the distance and relative position of which can be

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regulated at will. Fig. 33 shows the tubes in place and the experiment ready.

3. Now, if mixed dry nitrogen and oxygen, or even atmospheric air, are subjected to the action of a series of electric sparks, after a few minutes the test-tube is filled with nitrous vapour, but it would need several hours to arrive at the limit of the reaction. This is, moreover, never complete, the spark inversely decomposing nitric peroxide (see p. 198).

4. If the operation take place in presence of a solution of potash, the acid gases are gradually absorbed and potassium nitrate is finally obtained. This is Cavendish's celebrated experiment (1785).

5. The combination of nitrogen with oxygen requires the intervention of a foreign energy represented by $-21{\cdot}6$ Cal., when the union of nitrogen with oxygen takes place, forming nitric oxide—

$$N + O = NO.$$

The latter compound afterwards unites with an excess of oxygen, forming nitric peroxide.

The definitive formation,

$$N + O_2 = NO_2 \text{ gaseous},$$

only corresponds to an absorption of $-2{\cdot}6$ Cal. at the ordinary temperature, a quantity which increases to about -7 Cal. towards 200°.

6. It is precisely in virtue of analogous reactions developed in the atmosphere during the passage of forked and sheet lightning that nitric and nitrous acids are formed. These acids appear in rainstorms, partly in the free state and partly as ammonium nitrate or alkaline nitrates, the latter being derived from the dust of the air. For example, Filhol, at Toulouse, obtained per cubic metre of rain, 1·09 grms. of nitric acid. From the analyses of M. Barral, one hectare of ground at Paris would have received in November, 1852, from the rain, 659 grms. of nitrogen in the form of nitric acid. These quantities are considerable, nevertheless the analysis of cultivated plants has shown that they do not suffice to make good the losses of nitrogen taken from the soil by vegetation.

Fourth Section.—Actions of the Silent Discharge at High Tension.

1. The *combination of nitrogen and oxygen* with the formation of nitrous compounds is not only produced by the electric spark, but also by the action of the silent discharge, when the electric tension is very great (see the instruments, pp. 226 and 230).

2. This is, again, a condition which occurs in the atmosphere. During the interval of time which precedes the instant when the discharges of lightning, properly so called, trace a certain

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line in the atmosphere, there are very widespread surfaces which gradually become electrified by influence, then suddenly discharge themselves at the moment of the explosions (return shock). Over these electrified surfaces there are exerted certain chemical reactions analogous to those developed by the silent discharge at a high tension and with a suddenly varying potential. These are, moreover, accidental, local, and momentary effects, as well as those of lightning properly so called. It is probable that they are especially produced on mountains and isolated peaks.

3. The electric influence thus causes the formation of hyponitric and nitric acids, and even that of pernitric acid,[1] an unstable compound produced by the reaction of the silent discharge at a high tension on a mixture of hyponitric acid and oxygen.

4. *Nitrogen and water.* Under the influence of high electric tensions, free nitrogen and water combine to form ammonium nitrite, according to the author's experiments[2]—

$$N_2 + 2H_2O = NH_4NO_2,$$

the energy necessary for this reaction ($-$ 73·2 Cal.) being supplied by electricity.

5. The effects just described are produced under the influence of external discharges of the Ruhmkorff coil, the potential of the electrified bodies thus passing in a very short interval of time through all values, from zero to a limit amounting to several thousand volts.

6. The same effects also take place, each pole being alternately charged with positive and negative electricity, as with the Ruhmkorff coil, or each pole being constantly charged with the same electricity, as may be obtained by the Holtz machine.

7. But these reactions gradually become weakened if the potential be lowered, and finally cease entirely, when it falls below a certain limit, relatively very high, that is, reaching to several hundred volts. Below this limit nitrogen and oxygen cease to combine, although ozone is still formed.

8. It should be noted that this limit of potential is far higher than the ordinary tensions which atmospheric electricity can assume, except in stormy weather. The direct formation of the oxygenated compounds of nitrogen in nature is, therefore, limited to the conditions of very great electric tension and the influence of storms.

9. We will examine, from the same point of view, the *combination of nitrogen with hydrogen;* that is to say, the formation of ammonia by the action of electricity.

[1] "Annals de Chimie et de Physique," 5e série, tom. xxii. p. 432. The author had noticed the formation of the last combination; but it has been demonstrated in a more complete manner and studied more particularly by Chappuis and Hautefeuille.

[2] Same collection, 5e série, tom. xii. p. 455.

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Take, first, the action of the spark. It is well known that ammonia is decomposed by a series of sparks into its elements, the volume of the gas being practically doubled after a rather short period of time. Nevertheless, there remains a trace of ammonia, not capable of measurement, though capable of being manifested, as will be presently shown. Now, nitrogen and hydrogen undergo reciprocally a commencement of combination, by the action of a series of electric sparks. However, the proportion of ammonia formed is so slight as not to be shown by a change in volume. But it is sufficient to introduce into the gases a bubble of hydrochloric acid gas to produce abundant fumes. (In order that the experiment may be reliable, it is necessary to operate with gases thoroughly dried before the experiment and over dry mercury, the least trace of water vapour being indicated in the same way by hydrochloric acid gas.) This reaction is so delicate that it reveals the thousandth part of a mgrm. in a small volume of gas.

To accumulate the effects of this reaction, it is sufficient to operate in presence of dilute sulphuric acid, so as to gradually absorb the ammonia. It is then easy to collect a considerable quantity of it at the end of a sufficient time. The author has not been able to discover the inventor of this experiment, but it appears as already classic in the first edition of Regnault's "Traité de Chimie," printed in 1846, and dates from still further back.

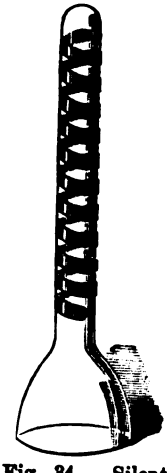

Fig. 34. — Silent discharge test-tube.

10. The action of the silent discharge is far more efficacious than that of the spark in causing the union of nitrogen with hydrogen.

The silent discharge has also the double property of decomposing ammonia into its elements and of combining elementary nitrogen and hydrogen. These two gases being mixed in the ratio of three volumes of hydrogen to one volume of nitrogen, if the silent discharge be made to act upon the mixture, after a few hours as much as three per cent. of the mixture will be found to have been transformed into ammonia. The latter may then be measured by volume, and manifested by all its reactions.

11. The apparatus which was most commonly employed for making the silent discharge act upon the gases is formed of two distinct glass tubes—

(1) A very thin stoppered tube, enlarged at the lower part, and forming a test-tube, so arranged as to permit of the introduction, the extraction, and the rigorously exact measurement of the gases over mercury, all as clearly and easily as with ordinary gas test-tubes.

This tube is surrounded by a thin strip of platinum, arranged

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spirally on its external surface (Fig. 34), this strip being fixed with gum. The whole glass surface in contact with the atmosphere is carefully coated with shellac, in order to insulate it more fully.

(2) A V tube (Fig. 35), slightly less in diameter than the test-tube, so arranged as to be able to be introduced into it, almost without friction.

This tube is closed at one of its ends (Fig. 35), and filled with dilute sulphuric acid.

The test-tube being placed over a large mercury trough, the gases on which it is desired to operate are introduced into it after having been measured in a graduated test-tube with the usual precautions. The volume is regulated according to the capacity of the test-tube, diminished by that of the vertical portion of the V tube. It is also necessary to take account of the increase of volume produced by decomposition, if there be occasion to do so. The closed part of the V tube is then introduced into the interior of the test-tube, first having been filled with water acidulated with sulphuric acid.

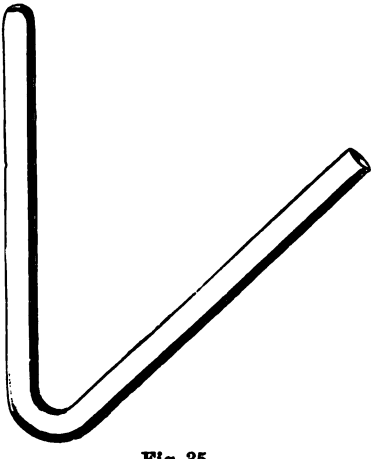

Fig. 35.

Then, the test-tube being held in the left hand, a small porcelain basin, like those usually employed for measuring nitrogen in organic compounds, is introduced by the right hand under the mercury, and passed under the test-tube, held vertically, when the whole is taken away, so as to isolate the test-tube arranged over the basin, as in Fig. 36.

It is held in place with the aid of the wooden jaw of a Gay-Lussac support, which, for the sake of simplicity, has not been shown. This support, at the same time, applied against the platinum strip in Fig. 36, keeps in place a thin sheet of platinum, fixed at the end of a wire communicating with one of the poles of a very large Ruhmkorff coil, whilst the other pole is attached to a second wire which dips into the acidulated water of the V tube.

12. The combination of nitrogen with hydrogen, as well as that of oxygen and nitrogen, ceases below a certain potential of the electric apparatus, which produces the silent discharge. It does not take place at all at the low tensions.

13. *The combination of free nitrogen with the hydrocarbon*

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compounds is of great importance. Before the author's experiments it was entirely unknown. It is a remarkable circumstance that this combination takes place equally well with the highest and even the lowest electric tensions, contrary to what happens in the case of oxygen and hydrogen. The products, moreover, vary according to the greatness of the electric tensions.

14. *Hydrocyanic acid.* In allowing the voltaic arc or the electric spark to act directly upon gases, the author has observed that acetylene and nitrogen combine directly at equal gaseous volumes, forming hydrocyanic acid. The same reaction takes place with every hydrocarbon gas or vapour capable of forming acetylene under the influence of the spark. This formation of

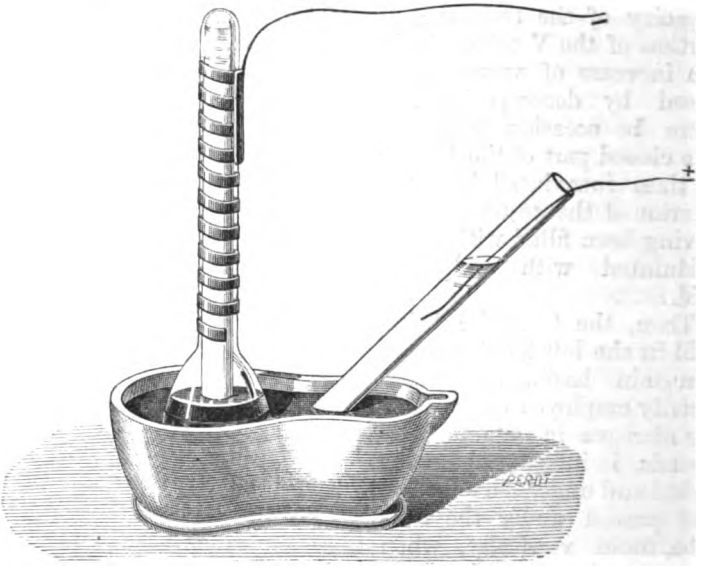

Fig. 36.—Action of the silent discharge on mercury.

hydrocyanic acid constitutes the best defined positive character of nitrogen and is the easiest to show.

If a series of strong sparks be passed into a mixture formed by the two pure gases, the gases assume almost immediately the characteristic odour of hydrocyanic acid.

After a quarter of an hour, or even less, if the sparks are long and strong the reaction is already well advanced. It is then sufficient to agitate the gas with potash to change the acid into alkaline cyanide and to manifest the reactions which are characteristic of it (Prussian blue, etc.)

Under the circumstances just described the formation of hydrocyanic acid is accompanied by that of carbon and hydrogen, formed in virtue of a distinct but simultaneous decomposi-

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tion of the acetylene. But this complication may easily be avoided by adding beforehand to the mixture a suitable volume of hydrogen, for instance, ten times the volume of the acetylene; no further deposit of carbon is then observed, and the reaction absolutely corresponds to the following equation :—

$$C_2H_2 + N_2 = 2CNH.$$

The presence of the hydrocyanic acid formed is not, however, completely accomplished under the conditions just described, and the reaction ceases at a certain limit, because the hydrocyanic acid is inversely decomposed by the spark, into nitrogen and acetylene. But if the hydrocyanic acid be gradually removed by potash, care being taken to dry the gases each time, before renewing the action of the spark, a given volume of nitrogen may be completely transformed into the acid, as has been expressly verified. Hydrocyanic acid is formed solely by the action of the spark or arc, and not of the silent discharge.

15. *Nitrogen and organic compounds.* Nevertheless nitrogen is also absorbed by organic matters, when operating with the silent discharge by means of a powerful Ruhmkorff coil and the test-tube just described. It is easy to observe (at an ordinary temperature) the absorption of a measurable volume of nitrogen either by hydrocarbons (benzene, essence of turpentine, etc.), or by ternary substances, such as ether, moist dextrine, or paper.

16. *Nitrogen and hydrocarbons.* The experiment is very well defined with *benzene*, a compound devoid of oxygen, 1 grm. of benzene absorbing in a few hours 4 to 5 cub. cms. of nitrogen, the greater part remaining unaltered. The reaction is effected principally between electrified benzene, in vapour, or under the form of very thin liquid layers, and nitrogen gas. It gives rise to a polymeric and condensed compound, a sort of solid resin, which collects on the surface of the glass tubes through which the discharge is effected. This compound, when highly heated, is decomposed, with liberation of ammonia. But free ammonia does not pre-exist, nor is it formed by the *silent discharge*, either in the dissolved state in the excess of benzene, or in the gases. The latter, moreover, contain a little acetylene, which appears constantly in the reaction of the silent discharge on the hydrocarbons. *Essence of turpentine* also gave rise to an absorption of nitrogen, in reality slower under the same conditions. There was also produced a condensed resinous body, which liberates ammonia on ignition.

The *vapour of ether* also absorbs nitrogen. Methane behaves in the same manner. It yields at once (in a small quantity) a very condensed solid nitrogenous product, which liberates ammonia, by heat, and free ammonia, which remains mixed with the non-condensed gases. With *acetylene*, the principal

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product is a polymeric substance, discovered by Thenard. Nitrogen and acetylene, moreover, do not form hydrocyanic acid under the influence of the silent discharge, a result which contrasts with the abundant formation of this compound under the influence of the spark. However, the condensed product formed by acetylene modified in presence of nitrogen, when subsequently destroyed by heat, liberates towards the close some traces of ammonia.

17. *Nitrogen and carbohydrates.* The following are various experiments relative to the absorption of nitrogen by the action of the silent discharge at high tension, which are calculated to show that this absorption really takes place, when operating with the principal constituents of vegetable tissues, either with pure nitrogen or in presence of oxygen, that is, by bringing atmospheric air into action.

White filter paper (cellulose or ligneous principle) slightly moistened and submitted to the influence of the silent discharge, in presence of pure nitrogen absorbs a very marked quantity of it in the space of eight to ten hours. It is sufficient to heat the paper strongly afterwards with soda-lime, to liberate from it a great quantity of ammonia. The original paper did not appreciably yield any under the same conditions. Ammonia, besides, is only produced towards a dull red heat by the destruction of a particular and fixed nitrogenous compound, as with the hydrocarbons.

18. The presence of oxygen does not prevent this absorption of nitrogen. The following experiment shows this. The glass tubes through which the electric influence is exerted having been covered with a thin coat of a syrup-like solution of dextrine (a few decigrammes in all), a certain volume of atmospheric air was introduced into them over mercury.

After having made the silent discharge act for about eight hours, an absorption of 2·9 per cent. of nitrogen and 7·0 of oxygen in 100 volumes of the original air was observed. It will be seen that the absorption of the oxygen was not total under these conditions. As a check the organic matter remaining on the surface of the tubes was collected and heated with soda-lime, it liberated ammonia in great abundance and only towards a dull red heat, which completes the demonstration. For the rest, it was not found that free ammonia, nitric or nitrous acids were formed in any appreciable amount, at least under these conditions.

19. The principal phenomenon is therefore the production of a complex nitrogenous compound by the direct union of free nitrogen with the carbohydrate experimented upon, a reaction perfectly comparable to those which must be produced in nature, by the contact of vegetable matter with the electrified atmospheric air.

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20. The absorption of nitrogen by organic compounds takes place likewise under the *influence of both kinds of electricity.* It takes place in just as well defined a manner with the lowest as with the highest tensions, but in a time which is the longer, the lower is the electric tension. It is very marked even with the low tensions which no longer yield the oxides of nitrogen. This absorption has been verified, both by insulating the silver or platinum [1] armatures held in contact with the paper and the gases, and also by insulating the paper itself from all metallic contact between two glass surfaces. At the same time as the fixed nitric compounds already referred to, and under these conditions, *no trace of ammonia was formed, and no trace of nitric or nitrous acid, or of hydrocyanic acid.*

21. Working under similar conditions, and with very low tensions, it was found that the fixation of the nitrogen was especially abundant with paper, less with ether, and still less with benzene, a diversity corresponding to the unequal stability of these principles and to the different nature of the nitrogenous principles derived from them. With paper especially, there are produced at the same time insoluble nitrogenous compounds, very slightly coloured, which remain fixed upon the woody fibre, and nitrogenous bodies which are soluble in water and almost colourless, which are condensed upon the sheet of platinum; the latter contain such large quantities of nitrogen that they yield free ammonia which turns litmus paper blue, even without any addition of soda-lime.

22. The experiments just described define the general conditions of the chemical reactions produced by the silent discharge, but they do not indicate clearly the effects of the electrical tension, free from all complications. In fact, in the experiments made with the help of the Ruhmkorff apparatus, or the Holtz machine, the tension changes continually during the interval between the outer sparks, and this between limits that vary by several thousand volts.

What is the influence of these incessant variations and the sudden alternations accompanying them? Are the chemical reactions determined by the very fact of these alternations and the molecular shocks and vibrations resulting from them, or can the chemical reactions be produced by a simple difference of potential, or a simple determination of the gaseous molecules,

[1] The metallic armatures had been brought to a red heat in the open air before each experiment in order to destroy every trace of organic matter on their surfaces. Care must be taken not to touch them with the fingers. The Swedish paper and the dextrine employed did not contain more than a ten-thousandth part of nitrogen according to a special analysis, a proportion which is of no account when a few centigrammes of paper are operated upon. This verification must be made each time upon strips taken from the same sheet of paper and in an alternate manner, the paper sometimes accidentally containing nitrogenous substances.

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without there being either any voltaic current properly so called, as with a closed battery, or elevation of temperature, as with the spark, or sudden and incessant variations of tension, as with the silent discharge developed under influence of the Holtz or Ruhmkorff machines? The following experiments were made in order to solve these questions.

Fifth Section.—Action of Electricity at very Low Tension.

1. These fresh trials were made with a battery, *without closing*

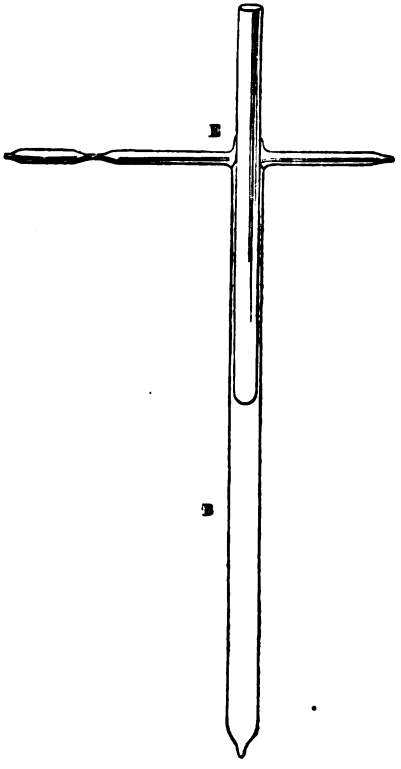

Fig. 37.—Apparatus open.

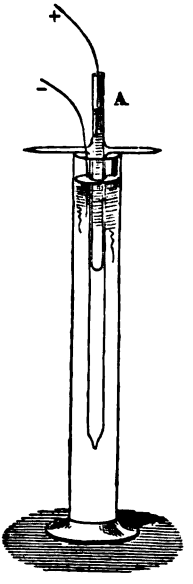

Fig. 38.—Apparatus arranged for the experiment.

the circuit, and under such conditions that the entire experiment resolved itself into the establishment of a constant difference of potential between the two armatures. This difference was measured by the electro-motive force of five Leclanché cells (a force equivalent to about seven Daniell cells) in the greater number of the experiments about to be described. Each experiment lasted from eight to nine consecutive months.

2. Metallic armatures had to be given up on account of the special reactions they bring about, and it was necessary to

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place the gases in the annular space separating two concentric glass tubes fused together at the top.

The apparatus is shown on the preceding page. The inner tube is open and filled with dilute sulphuric acid; the outer one is closed at the blowpipe, and plunged into a test-glass containing the same acid. The gases and other bodies are introduced beforehand into the annular space, by means of small tubes, which are then closed at the blowpipe.[1] The positive pole of the battery is put in communication with the acid liquid of the inner tube, which acts as armature; and the negative pole with the acid liquid of the test-tube, which acts as a second armature, separated from the first by a dielectric formed of two thicknesses of glass and the gaseous stratum between. The gases are thus contained in a space completely closed by fusion of the glass without any metallic contact.

3. The following results were observed under these conditions: the formation of ozone, into which it is not necessary to enter here; the absorption of the free nitrogen by the paper and by the dextrine; and the formation of special nitrogenous compounds, exactly as in the experiments on p. 229.

4. Some of the experiments were made under quantitative conditions, so as to measure the weight of nitrogen absorbed in a given time. For this purpose over half the outer surface of a large cylinder of thin glass, A, terminated by a spherical cap, a sheet of Swedish paper, weighed beforehand and damped with pure water, was laid. The other half of the same outer surface was coated with a syrupy solution of dextrine tested and weighed under conditions that enabled us to know exactly the weight of dry dextrine employed. The inner surface of the cylinder had been covered beforehand with a sheet of tinfoil (internal armature). This cylinder was placed upon a glass plate, and then covered over with a concentric cylinder of thin glass, B, as closely as possible, the inner surface of this cylinder being left uncovered, and the outer surface covered with a sheet of tinfoil (external armature).

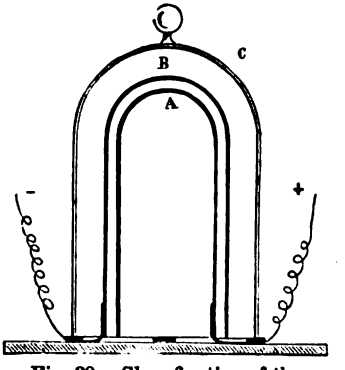

Fig. 39.—Slow fixation of the nitrogen.

The system of two cylinders was covered with a bell-glass, C, to keep out dust, and placed upon a glass plate, arranged so as to keep the apparatus airtight.

The internal armature was put in communication with the positive pole of a battery formed of five Leclanché cells, arranged

[1] "Annales de Chimie et de Physique," 5e série, tom. xii. p. 463.

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in series, the external armature with the negative pole of the same battery. In this way there was a constant difference of potential between the two armatures of tinfoil, separated by the two thicknesses of glass, by the stratum of air between, and lastly by the paper or dextrine applied to one of the cylinders. Before the experiment the nitrogen was estimated in the paper and in the dextrine (working upon two grammes of dry material), and was found to be, in 1000 parts—

Paper ·10, dextrine ·12.

At the end of a month (November), having worked at first with a single Leclanché element,

Paper ·10, dextrine ·17,

mould had formed. There being no variation in the paper and very little in the dextrine, the experiment was continued with five Leclanché cells for seven months, the outside temperature being raised little by little until at times it reached 30°. Again mould was observed. At the end of this period, in 1000 parts, the nitrogen was found to be—

Paper ·45, dextrine 1·92.

The space between the two cylinders was from three to four millimetres. Another trial, made at the same time, with nearly treble the space between two other concentric cylinders, similar to the first, gave, in nitrogen in 1000 parts—

Paper ·30, dextrine 1·14.

All these analyses go to establish the fact that there is a fixation of nitrogen upon paper and upon dextrine, *i.e.* upon vegetable substances that are not directly nitrogenous, under the influence of excessively low electrical tensions.

The effects are here provoked by the difference of potential existing between the two poles of a battery formed of five Leclanché cells, a difference that may be compared to atmospheric electricity acting at short distances from the earth.

5. The influence of the mould, observed in the course of the experiments, cannot be taken into account, for Boussingault has proved, by very careful analysis,[1] that this vegetable substance does not possess the power of fixing atmospheric nitrogen.

6. The influence of light did not enter into the above experiments, in which the fixation of the nitrogen was effected in total darkness. Other experiments, however, performed in the light, showed that light does not impede the electrical fixing of the nitrogen.

7. The reactions just described are determined by very low electrical tensions, the value of which is quite comparable to those of atmospheric electricity, as is shown by the measure-

[1] "Annales de Chimie et de Physique," 3e série, tom. lxi. p. 363.

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ments published by Thomsen, Mascart, and various other experimentalists.

8. In order to complete this demonstration, it was thought expedient to operate upon *atmospheric electricity itself*. For this purpose, the author worked by means of the difference of potential existing between the earth and a stratum of air about two metres above it in the garden of the observatory at Montsouris.

The results obtained, during experiments which lasted from July 29 to October 5, 1876, *i.e.* rather more than two months, will now be given, the mean electrical tension having been about that of three and a half Daniell cells, and having fluctuated in absolute value from + 60 Daniell to about − 180 Daniell, in the apparatus.

In all the tubes, without exception, whether they contained pure nitrogen or ordinary air, whether they were hermetically sealed or in free communication with the atmosphere, the nitrogen fixed itself upon the organic substance (paper or dextrine), forming an amide compound, which was decomposed by soda-lime at about 300° to 400°, with regeneration of ammonia.

The same substances, left freely exposed to the atmosphere of a room apart from the laboratory, did not give the least sign of the fixation of nitrogen.

The quantity of nitrogen thus fixed under the influence of atmospheric electricity is, moreover, very small in each tube. This may be explained by the smallness of the weight of organic matter (a few centigrammes), by the slowness of the reactions, and lastly by the limited extent of the surfaces influenced.[1] As, however, the number of tubes capable of being arranged in the same circuit might certainly be very much increased, without affecting the electrical effects any more than the chemical effects derived from them, we see that the quantity of nitrogen capable of being deposited on a surface covered with organic matter at the end of a suitable time may be rendered considerable without any other depositing influence being brought to bear upon it than the natural difference of potential between the earth and the strata of air two metres above it. We thus find ourselves in conditions similar to those of vegetation increased in the relation existing between the distance from the outflow tube in the Thomsen apparatus to the earth and the distance between the two armatures of the author's tubes.

[1] No trace of nitric acid was found either in the water which had been in contact with the organic substances, or in special tubes containing only air and water and subjected simultaneously to atmospheric electricity. The silent discharge under these conditions of feeble tension does not, therefore, seem to determine the union of the nitrogen with oxygen, so as to form nitric acid.

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9. Two of the experiments enable the demonstration to be carried even further. In fact, the damp paper contained in two tubes (nitrogen with an armature of silver in the inner tube, air with an armature of platinum in the annular space) was found to be covered with greenish stains, formed of microscopic algæ, with fine filaments interlaced and covered with fructifications. They derived their origin, no doubt, from some germs introduced accidentally before the closing of the tubes. Now, in these two tubes there was much more nitrogen fixed than in tubes deprived of vegetable matter. In the nitrogen tube especially, the gases emitted a sourish and slightly fœtid odour, similar to that of certain fermentations, and the deposition of nitrogen was much greater than in any of the others.

10. From these facts it follows that the deposition of nitrogen in nature, which is indispensable for the formation of nitrates, and also for the development of vegetable life, may take place directly and under normal atmospheric conditions, without necessarily being correlative either with the formation of ozone or with the previous production of ammonia or nitrous compounds; this last-named production only taking place with the help of stormy and exceptional tensions.

We know, however, that working in a closed space, Boussingault, whose ability is well known, did not succeed in proving the absorption of free nitrogen. But atmospheric electricity at a low tension did not act in these experiments *in vitro*, in which the potential is the same at all the internal points of the apparatus, and its intervention is apparently of a nature to modify the conclusions of this eminent authority.

11. The result of the author's experiments is to show clearly the influence of a new natural cause, an influence of great importance to vegetation. Up to the present, whenever the question of atmospheric electricity has been studied from an agricultural point of view, only its luminous and violent manifestations have been considered, such as thunder and lightning. Even the action in nature of those high tensions which determine the formation of nitrous compounds by influence had scarcely been taken into consideration before the author's experiments (p. 215).

In all cases, only the formation of nitric and nitrous acids and of ammonium nitrate was studied. The author considers that up to the present there has been no other suggestion made with regard to the influence of atmospheric electricity being capable of constituting the distant and indirect source of the fixing of nitrogen on vegetable substances. Before the experiments just described, there was no idea of the direct reactions that can take place between vegetable matter and atmospheric nitrogen under the influence of feeble electrical tensions. The starting into activity of the nitrogen under these feeble

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tensions is, however, of great interest, and it is these feeble tensions that seem to be the most efficacious, the slightness of the effects being compensated by their duration and by the vast extent of the surfaces influenced. We have to do with quite a new kind of action, until now completely unknown, which is working incessantly under the most unclouded sky, to determine a *direct* fixing of nitrogen upon vegetable tissues. In studying the natural causes capable of acting upon the fertility of the soil, and upon vegetation, causes which it has been sought to define by meteorological observations, we must for the future take into consideration not merely luminous or calorific influences, but also the electrical condition of the atmosphere.

12. We will now specify more particularly the character of these reactions in nature. When studied at a given spot, and over a small surface, they can certainly be only very limited, otherwise the humic substances in the soil would rapidly become rich in nitrogen; whereas the regeneration of naturally nitrogenous substances, when exhausted by cultivation, is, on the contrary, as we know, excessively slow.

But this regeneration is indisputable, for in no other way can we account for the unlimited fertility of soils that receive no manure, such as the meadows on high mountains, as studied by Truchot, in Auvergne.[1]

It will be remembered that Messrs. Lawes and Gilbert, in their celebrated agricultural experiments at Rothampstead, came to the conclusion that the nitrogen in certain crops of leguminous plants exceeds the sum of the nitrogen contained in the seed, the soil, and in the manure, even adding the nitrogen supplied by the atmosphere under the known form of nitrates and ammoniacal salts; a result which is all the more remarkable, seeing that a portion of the nitrogen combined is eliminated in a free state during the natural transformations of vegetable products. We observe, therefore, only the difference between these two effects, *i.e.* that the actual fixing of nitrogen is much greater than the apparent. In most cases it is concealed by the causes of loss. The above-mentioned writers concluded from their observations that there must exist in vegetation some source of nitrogen sufficient to account for the great mass of combined nitrogen in existence on the surface of the globe. But the source of this was until now quite unknown. Now, it is precisely this hitherto unknown source of nitrogen that would seem to be established in the author's experiments on the chemical reactions provoked by electricity at low tensions, and especially atmospheric electricity.

13. To complete this explanation, we will compare the quantitative data of the experiments with the richness in nitrogen of the vegetable tissues and organs that are renewed

[1] "Annales agronomiques," tom. i. pp. 549 and 550. 1875.

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each year. The leaves of trees contain about ·008 of nitrogen, wheat straw about ·003.

Now, the nitrogen fixed upon the dextrine, in the experiments, at the end of eight months, amounted to about ·002 (p. 232), *i.e.* a nitrogenous substance was formed of a richness almost comparable to that of herbaceous tissues, produced in vegetation in the same space of time, with the help of the influences exercised by natural electrical tensions, which may be compared to those of the foregoing experiments.

14. This new cause of the fixing of the atmospheric nitrogen in nature is of the highest importance. It engenders condensed nitrogenous products of the humic order, so widely diffused over the surface of the glode. However limited the effects may be at each moment and at each point of the terrestrial superficies, they may, however, become very considerable, on account of the extent and continuity of a reaction working universally and perpetually.

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CHAPTER VI.

THE HEAT OF FORMATION OF HYDROGENATED COMPOUNDS OF NITROGEN.

§ 1. Heat of Formation of Ammonia.

1. The heat of formation of ammonia, of nitric oxide, of water, of carbonic acid, and of hydrochloric acid, constitute, perhaps, the most important data of thermo-chemistry. The three last have been, for the last forty years, the subject of numerous direct measurements on the part of the most skilled experimentalists; they may therefore be looked upon as known within one or two per cent. of their absolute value. In the foregoing chapter the heat of formation of nitric oxide has been given, and we may now proceed to study that of ammonia. Before the author's last researches it was only known in a somewhat unsatisfactory manner; two measurements only had been taken of it, and these by an indirect process without control.

2. It is by making chlorine act upon diluted ammonia, and then weighing the chlorine absorbed, that Favre and Silbermann, and afterwards Thomsen, endeavoured to estimate the heat of formation of ammonia. They assumed that the reaction worked upon the whole of the chlorine according to the following formula, which is admitted in the elementary treatises, but in none of these works is the quantitative realisation of this equation verified by the calorimeter—

$$4NH_3 \text{ dilute} + 3Cl \text{ gas} = N \text{ gas} + 3NH_4Cl \text{ dilute}.$$

Favre and Silbermann obtained results which, for fourteen grammes of nitrogen, gave—

$$N + H_3 = NH_3 \text{ gas} + 22{\cdot}73 \text{ Cal.}$$
$$N + H_3 + \text{water} = NH_3 \text{ dissolved} + 31{\cdot}47.$$

Thomsen, having repeated the same experiment, obtained different results—

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$$N + H_3 = NH_3 \text{ gas}, + 26{\cdot}71 \text{ Cal.}$$
$$N + H_3 + \text{water} = NH_3 \text{ dissolved}, + 35{\cdot}15 \text{ Cal.}$$

The difference is considerable, amounting to 4 Cal., or nearly 20 per cent. Thomsen tried to reconcile these figures by recalculating the figures of Favre and Silbermann, according to his own data regarding the heat of formation of hydrochloric acid and ammonium chloride. But corrections of this kind are very problematical,[1] seeing that the figures of the above-mentioned writers form a complete whole: the cause of the divergence is apparently quite a different one.

3. In fact, some years ago, the author began to doubt the accuracy of all these figures, in the course of his studies of the heat of formation of the oxygen acids of the halogen elements.[2] Having measured that of the hypobromites, he thought it might serve to determine that of urea, in accordance with the process of analysis generally followed for that substance. But it was desirable first to verify the reaction of the hypobromites upon ammonia itself, and it was then found that extraordinary losses of heat took place, quite irreconcilable with those that could be calculated from the data that have been accepted with regard to ammonia. The experiments were made, starting with pure liquid bromine of a determined weight. It was dissolved in a weak solution of soda, and the heat liberated was measured; then weak ammonia was also added in considerable excess, and the second escape of heat was measured. The total result must represent the transformation of the bromine, ammonia, and soda into sodium bromide, water, and nitrogen—

$$6Br + 2NH_3 \text{ dilute} + 3Na_2O \text{ dilute} = 6NaBr + 3H_2O + N_2.$$

This is the thermal result observed, as obtained from the effect of the two operations, performed one after the other—

$\frac{1}{2}$(6Br acting on $3Na_2O$) dilute	+ 18·0
NH_3 dilute acting on the hypobromite	+ 88·8
Total	+ 106·8

[1] It would at least be as reasonable to correct Favre and Silbermann's results by the following considerations. Their data were almost all obtained with the mercury calorimeter; now the unit employed by them in this instrument was apparently too high by about one-tenth, according to the error that they committed in the estimation of the heat of neutralisation of nitric acid, hydrochloric acid, etc. All the quantities that enter into the calculation of the heat of formation of ammonia, and consequently this heat of formation itself, should therefore be reduced in the same proportion.

[2] "Annales de Chimie et de Physique," 5ᵉ série, tom. v. p. 333, hypochlorites; tom. x. p. 377, chlorates; tom. xiii. pp. 18 and 19, bromates et hypobromites; p. 20, iodates. See Book II. chap. XII. of the present work.

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If we admit the preceding reaction, we shall take—

As the initial condition		$\frac{1}{2}$(6Br + 6H + 2N + $3Na_2O$ dilute)
Final condition	...	$\frac{1}{2}$(6NaBr dissolved + $3H_2O$ + N_2)

First Cycle.

$\frac{1}{2}$[6(H + Br) + water = 6HBr dilute] ...	...	...	+ 88·5 (B)
$\frac{1}{2}$[6HBr dilute + $3Na_2O$ dilute] ...	...	...	+ 41·1 (B)

Second Cycle.

N + H_3 + water = NH_3 dilute ...	...	...	...	x

Successive reactions of the bromine upon the soda and of the hypobromite upon the ammonia, + 106·8, whence we get $x = +22·8$ in place of +35·15 or 31·5. The same experiment, repeated with potash and with baryta, gave similar results. It was proved, moreover, by collecting over mercury the nitrogen set free, that the reaction differs little from the above equation; in fact, the volume of nitrogen given off amounted to about nine-tenths of the theoretical value, a secondary phenomenon[1] having abstracted from the fundamental transformation a portion of the bromine employed.

Whatever hypothesis may be formed as to the missing tenth, we cannot explain the difference between 35·15 and 22·8.

In other words, these experiments, which are very simple and easily executed with the calorimeter, gave 12·35 Cal. more than were indicated by the received numbers; an excess which is too great to be explained by any error in the experiments. However, even the heat of formation of the ammonia does not come out with sufficient accuracy in these trials; fearing, therefore, some mistake in such an important question, the further study of this subject was postponed. It was, however, recently resumed, with the following results.

4. It was first attempted to determine whether chlorine, in the presence of dilute ammonia, really decomposes it without heat, with the immediate liberation of a quantity of nitrogen equal to the chlorine employed. The experiment is easily made. We require merely to pass a known volume of chlorine (displaced in a gasometer by a flow of concentrated sulphuric acid) through diluted ammonia, taken at the surrounding temperature and enclosed in a small receiver, so as to collect the gases given off. It was found in two experiments made with an excess of ammonia (which is necessary in order to avoid the formation of nitrogen chloride)—

Chlorine 140 cc., nitrogen 20·5 cc., instead of 46·7 cc.
„ 243 „ „ 32 „ „ 81 „

[1] The formation of a small quantity of bromate?

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Moreover, these figures vary considerably, according to the conditions of the experiments, as might be expected. It would be easy to reduce them still further, and perhaps even to annul them altogether, by taking precautions to diminish the elevation of temperature developed upon the first contact of the chlorine with the ammonia, a diminution which was not attempted by any special contrivance. As they are, these numbers are in relation to the same conditions in the calorimetric measurements, and they are sufficient to establish the incomplete character of the reaction.

The liquids thus subjected to the action of chlorine contain ammonium hypochlorite, a compound previously mentioned by Balard and by Soubeyran, who had prepared it, the one with hypochlorous acid, the other with chloride of lime. The presence of hypochlorous acid may, in fact, be manifested in it. Perhaps there are also some chloro-substitution bases, intermediate between nitrogen chloride and ammonia.

The above liquids are in an unstable condition; they are continually giving off nitrogen. We have merely to pour them off into another vessel or stir them with a rod in order to make them pass into the gaseous form. They are well adapted to the repetition of Gernez's elegant experiments. Even after a day or two, the slow liberation of the nitrogen continues.

The author tried whether he could obtain at one stroke the nitrogen in solution, by adding to the liquid an excess of hydrochloric acid. The liquid, which had at first furnished 32 cms. of nitrogen, gave off upon this second operation 38·6 cms.; in all, 70·6 cms. instead of 81 cms. This last deficit results either from the solution of a small quantity of nitrogen, owing to the great volume of the final liquid, or to some quantity of chlorine being employed in a secondary reaction, such as the formation of a little chlorate or perchlorate. However this may be, the facts above mentioned show the causes of the errors of the first experimentalists. The action of chlorine upon ammonia could not, at any rate under the conditions with which they worked, be employed for measuring the heat of formation of this substance.

The action of the hypobromites would seem to be preferable, judging from the measurement of the volume of nitrogen liberated. This reaction, however, was not wholly satisfactory. The object in view was arrived at by quite another method, which is very simple and apparently faultless, as regards the completeness of the reaction, the direct combustion of the ammoniacal gas was effected by means of free oxygen.

5. *Combustion of ammonia.* The combustion of ammoniacal gas in free oxygen is effected with the same facility as that of hydrogen. It may easily be performed in the glass combustion

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vessel described elsewhere,[1] and which has already been used by M. Ogier and the author for burning pure carbonic oxide, acetylene, olefiant gas, benzene, cyanogen, phosphuretted, arseniuretted and silicated hydrogen, for forming hydrochloric acid gas, etc. It is shown in the subjoined figure.

This reaction, when effected satisfactorily, produces only nitrogen and water, in accordance with the equation

$$2NH_3 + O_3 = N_2 + 3H_2O.$$

The greater part of the water is condensed in the combustion tube, and the surplus upon the solid potash in two consecutive U-shaped tubes. This surplus represents a very small proportion of the water formed, a proportion corresponding to the normal saturation with the vapour of water of the gases set free. Its gaseous form has been taken into consideration in the calculations. The weight of the water is furnished by the variation in the weight of the vessel (filled with pure oxygen) and of the U-shaped tubes. From this we deduct the weight of the ammonia consumed, 27 grms. of water being furnished by 17 grms. of ammonia.

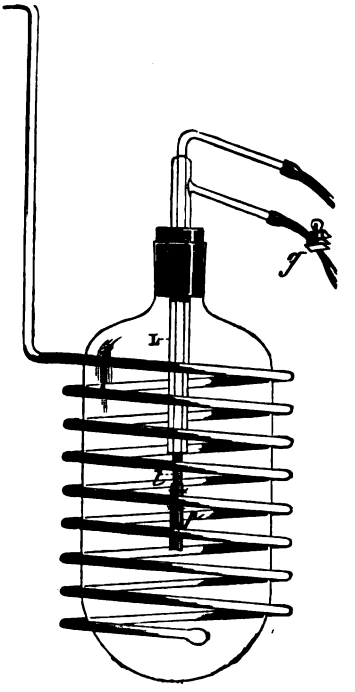

Fig. 40.—Combustion of ammoniacal gas.

The combustion should take place all at once and without relighting, an operation which necessitates the opening of the vessel and involves losses of watery vapour. If the condensed water shows any signs of the presence of the oxygen compounds of nitrogen, the quantity does not exceed some ten thousandths, that is to say, it may be disregarded.

The combustion of the ammonia, moreover, is complete, for no appreciable trace of it was found in the condensed water, and a tube of pumice-stone and sulphuric acid placed as a test at the end of the U-shaped tubes of solid potash, never increased in weight in the experiments.

These facts being stated, the following results were obtained under constant pressure, at about 12° :—

[1] "Essai de Mécanique Chimique," tom. i. p. 246.

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Weight of water obtained.	Heat given off as compared with 17 grms. = NH_3.
0·880 grms.	+ 91·1 Cal.
0·819 „	+ 90·7 „
1·004 „	+ 91·7 „
1·110 „	+ 91·4 „
1·006 „	+ 91·4 „
Mean	+ 91·3 „

The heat of combustion of ammonia in solution will thus be + 82·5.

6. It is easy to deduce from this the heat of formation of ammonia by its elements, without resting on any other basis than the heat of formation of water. This being admitted, according to the following data—

$$H_2 + O = H_2O \text{ liquid gives off } + 34{\cdot}5,$$

we deduce—

$$N + H_3 = NH_3 \text{ gas liberates } + 103{\cdot}5 - 91{\cdot}3 = + 12{\cdot}2.$$

The author found[1] that the solution of the ammoniacal gas in a large quantity of water gives off + 8·82. Thus—

$$N + H_3 + \text{water} = NH_3 \text{ dilute gives off } + 21 \text{ Cal.}$$

The value obtained with the hypobromite (+ 22·8) differs little from this; but it is necessarily less exact on account of the complication of the reactions.

The author therefore adopts the respective values of + 21 and + 12·2 for the formation of ammonia in solution and in the gaseous form.

Between the result + 12·2 and the figures + 26·7 previously adopted, there is a discrepancy of 14·5; this is the greatest experimental error that has up to the present been committed in thermo-chemistry. Its source has been shown, and it has been rectified accordingly.

7. Some months after the first publication of the results of the author's researches, Thomsen repeated the experiments, and he obtained for the heat of combustion of ammonia + 90·65, a value agreeing with + 91·3 within the limits of error allowed in experiments of this order. This is an important confirmation of the experiments. The heat of formation of ammonia seems, therefore, to be definitely fixed at + 12·2, or very near this.

[1] "Annales de Chimie et de Physique," 5e série, tom. iv. p. 526.

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§ 2. Heat of Formation of Ammoniacal Salts from their Elements.

1. The table of the heat of formation of the principal ammoniacal salts from their elements follows:

		Salts.	
		solid.	dissolved.
Chloride	$Cl + H_4 + N$	+ 76·7	+ 72·7
Bromide	Br gas + H_4 + N	+ 71·2	+ 66·7
„	Br liquid	+ 67·2	+ 62·7
„	Br solid	+ 67·1	+ 62·6
Iodide	I gas + H_4 + N	+ 56·0	+ 52·4
„	I solid	+ 49·6	+ 46·0
Sulphide	S gas + H_4 + N	+ 42·4	+ 39·2
„	S solid	+ 39·8	+ 36·6
Cyanide	C diamond + H_4 + N_2	+ 3·2	− 1·2
Nitrite	$N_2 + H_4 + O_2$	+ 64·8	+ 60·1
Nitrate	$N_2 + H_4 + O_3$	+ 87·9	+ 81·7
Perchlorate	$Cl + N + H_4 + O_4$	+ 79·7	+ 73·3
Sulphate	S solid + N_2 + H_8 + O_4	+ 141·1	+ 140·5
Bicarbonate	C (diam.) + N + H_4 + O_3	+ 205·6	+ 199·3
Formate	C („) + N + H_5 + O_2	+ 129·4	+ 126·5
Acetate	C_2 („) + N + H_7 + O_2	+ 159·6	+ 159·8
Oxalate	C_2 („) + N_2 + H_6 + O_4	+ 272·4	+ 264·4

2. The heat of formation of the same salts in a solid form, from ammoniacal gas and anhydrous or hydrated acids, taken in the gaseous form and in the solid form, has been given (p. 127).

3. We may also observe that the difference between the heats of formation from the elements, of anhydrous salts of potash and ammonia formed by strong acids, such as the nitrates, sulphates, perchlorates, is almost constant, being about + 30 Cal. But this difference decreases for weaker acids; it falls to 25 Cal. with the formates, oxalates, acetates, bicarbonates, etc.

§ 3. On the Volatility of Ammonium Nitrate.

1. It has been shown how ammonium nitrate may be decomposed in seven different ways, according to the process of heating (p. 5). Here certain experiments may be mentioned that indicate an eighth mode of action of heat, viz. the volatilization pure and simple of this salt.

2. Ammonium nitrate melts at about 152°, a temperature which the water, previously existing or formed by the decomposition of the salt, does not allow us to fix very accurately. It is only at 210° that it begins to decompose, that is, sufficiently to furnish an appreciable volume of gas in a few minutes, for the decomposition begins really at a lower temperature. This decomposition becomes more and more active, in proportion as

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the temperature of the salt melted is raised by some source of heat, without, however, the temperature being arrested at any fixed point between 200° and 300°. Pure nitrogen monoxide is thus given off.

But if we go on raising the temperature, the reaction becomes explosive at the time that the multiple products appear that are due to the many distinct modes of simultaneous decomposition, such as are shown on p. 5 of this work. All these phenomena are of the same order as those manifested generally by exothermal reactions, and their variety is a characteristic of explosive substances.

3. However, according to the author's experiments on the decomposition of ammonium nitrate, even with the greatest care, the quantity of nitrogen monoxide collected remains always considerably less than the theoretical quantity. This is on account of the volatility, real or apparent, of the ammonium nitrate. The difference is very great, even if we work with the lowest possible temperature, and in such a way as to prevent, as far as possible, the portions sublimed in the cold parts of the apparatus from gradually falling into the heated parts at the same time as the condensed water.

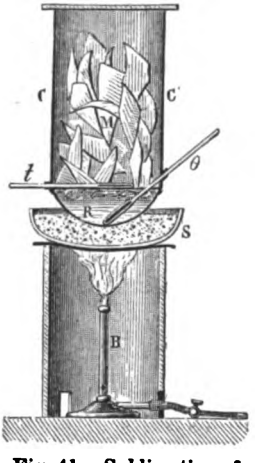

Fig. 41.—Sublimation of ammonium nitrate.

4. We can, in fact, sublime ammonium nitrate without destroying it to any extent (Fig. 41) by placing this salt, previously melted, in a capsule, R, which is closed by means of a sheet of blotting paper fastened over the top and surmounted by a cardboard cylinder, CC', the latter being filled with large pieces of glass. This is heated over a sand bath, S, by means of a Bunsen burner, B, properly regulated, care being taken that the temperature of the melted salt (which is shown by a thermometer, θ, plunged obliquely into it) does not exceed 190° to 200°. A very considerable proportion of the salt is then sublimed in beautiful brilliant crystals, adhering to the sides of the capsule and to the lower surface of the paper. A portion of the salt even passes through, and condenses above the capsule, in the form of a white smoke very finely divided and very difficult to collect.

At first, the existence of some special compound in this smoke, such as nitric amide, was suspected; but its identity with ammonium nitrate was proved by a complete analysis. The temperature of the paper thus traversed by the vapour may rise above 120 and even 130 degrees (as shown by a horizontal thermometer, *t*, laid upon the upper surface of the

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paper) without the paper being affected to any considerable extent. This experiment has some importance, as it shows that ammonium nitrate may be *volatilised as it is* without being at first resolved into ammonia and gaseous nitric acid—

$$NH_4NO_3 = HNO_3 + NH_3,$$

which would afterwards re-combine, the mixture when dissociated possessing all the energy of the simple components. In fact, we cannot understand how the vapour of nitric acid could be in contact with the paper, at a temperature which necessarily ranges between 130° and 190°, without oxidising it or destroying it instantaneously.

5. Ammonium nitrate, from the point of view of its volatility, and on account of many considerations, may be regarded as a typical explosive substance. In fact, pure nitroglycerin may also be evaporated without decomposition. Picric acid itself gives off very appreciable vapours, which sublime, and are condensed without alteration when the substance is heated with great care.

§ 4. Thermal Formation of Hydroxylamine or Oxyammonia.

1. We know that hydroxylamine is a product of reduction intermediate between hyponitrous acid and ammonia. It may be formed in a number of oxidations. It was thought expedient to determine its heat of formation, and this was done by decomposing its hydrochloride by means of a saturated aqueous solution of potash, very fine and very pure crystals of the salt being employed.

2. Hydroxylamine, exposed under these conditions, is immediately resolved into nitrogen and ammonia, according to M. Lossen's observations.

After having ascertained that no other product was formed (with the exception of a few hundredths of nitrogen monoxide) during the first moments of a sudden reaction, and that the proportion of hydroxylamine thus destroyed at the ordinary temperature and in a few minutes may amount to four-fifths of its total weight, the reaction was reproduced in the calorimeter, working with a known weight of hydrochloride, and collecting the gases given off over the water in the calorimeter itself, so as to measure them exactly.

3. We will now describe the apparatus employed in the experiments (Fig. 42).

(1) At the bottom of a large tube, TT, closed at one end, is placed a known weight of aqueous solution of potash, saturated at the temperature of the experiment.

(2) In this large tube is suspended above the potash a smaller tube, *tt*, containing exactly one grm. of hydroxylamine hydrochloride.

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(3) The small tube is wound round with a thick and heavy spiral of platinum, *gg*, intended later on to plunge the system below the level of the potash, and thus to determine the contact and the reaction between the alkaline solution and the solid salt.

(4) The upper end of this spiral is hooked on to a platinum wire $\frac{1}{20}$ mm. in diameter, stretched between the two copper wires of a small electric cable of gutta-percha, KK. This cable is intended to convey the current, which is to heat to redness and finally melt the little platinum wire, allowing the small tube to fall into the solution of potash, where the salt will react after its submersion.

(5) The large glass tube, TT, is closed with a cork, through which on one side passes the cable which winds in and out until outside the apparatus, and through the other side is passed a tube, *dd*, used for the liberation of gases.

(6) This large glass tube, TT, and the tube *dd*, including the curved extremity of this latter, through which the gases are to escape, are contained together in a small bell glass rather wide and capable of containing 200 to 250 cms. of gas, a volume considerably larger than that of the gases given off in the reaction.

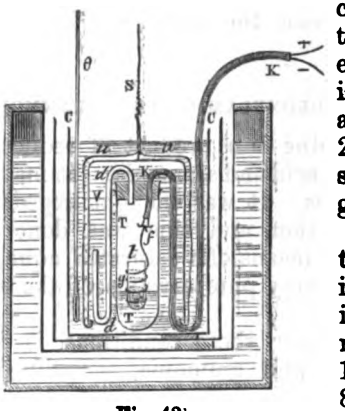

Fig. 42.

(7) This bell glass is in its turn placed upside down with its tubes and appurtenances, in an ordinary platinum calorimeter, CC, of a capacity of 1050 cms., but containing only 850 grms. of distilled water.

Thick copper wires, *uu*, arranged beforehand in the form of a star round a central point on the upper surface and on the axis of the bell glass, support it and keep it in a fixed position under the water. These wires are connected with a central rod, S, which rises vertically above the apparatus, and enables it to be attended to without any special instrument being introduced into the calorimeter.

It need not be said that the weight of each portion of this complicated apparatus was determined beforehand, so as to enable us to reduce the submerged masses to units of water. Moreover, special measurements of the specific heat of the cable and that of the cork were taken; these measurements may be made somewhat roughly, since the weight of the cable submerged does not exceed a few grammes; that of the cork is still less. As to the glass, copper, and platinum, their specific heat is known.

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(8) The parts being all adjusted, the air is exhausted in the bell glass by means of an inverted syphon.

(9) Then we have merely to follow the progress of the thermometer, θ, for ten minutes.

(10) We then heat and finally melt the little platinum wire by means of a current of four Bunsen elements, the hydroxylamine hydrochloride falls into the potash and is immediately destroyed. The gases produced by its destruction are given off under the bell glass. We give this glass a rotatory movement for a few minutes by means of the rod S, taking care to keep it completely submerged. Readings of the thermometer are taken every minute.

(11) This done, we break the bottom of the large glass tube by means of a platinum crusher introduced from outside and fixed at the extremity of a long rod of the same metal (Fig. 43); the liquids and other substances contained in the tubes spread out into the calorimeter and remain in it completely intermingled, this being effected by a suitable agitation which is easily performed by means of the rod S.

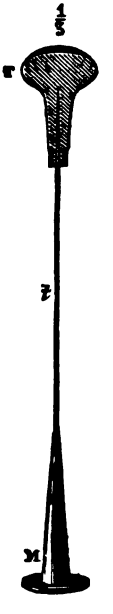

Fig. 43.—Platinum crusher.

(12) During this interval, and for a little while after, the progress of the thermometer is followed; all the thermal data are thus determined.

(13) This being done, all that remains is to know the volume of nitrogen developed by the decomposition. For this purpose we put the platinum calorimeter with the bell glass into the water contained in a very large earthen pan, so as completely to submerge them. The bell glass is then raised, so as to render it independent of the calorimeter, and the gases are transferred to a graduated testing apparatus.

These gases contain the nitrogen given off (mixed with three or four per cent. of nitrogen monoxide, according to the analyses), plus the air contained at first in the large tube and in the liberating tube. The volume of this air is known by the previous gauging of the tubes, if we deduct the liquid volumes of the potash and the various other objects introduced into the tube for the experiment. These volumes having been each measured separately, we succeed, finally, in ascertaining within about half a cubic centimetre the volume of nitrogen given off by the destruction of the hydroxylamine.

In the author's experiments this volume corresponded to 78 and 79 per cent. of the weight of the salt subjected to the reaction. The surplus of the salt, or more correctly the surplus of the hydroxylamine derived from it, is found unaltered in the

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water of the calorimeter, where it is mixed with the excess of potash.

The apparatus just described is very complicated, but the experiment is in itself very simple; it admits of a very accurate measurement of the heat given off, and the conditions at the commencement being ascertained with exactness, it is possible to arrive at a strictly definite final condition in one operation.

4. In order to calculate the decomposition of pure hydroxylamine, it is necessary to measure—

(1) The total heat given off in the reaction just described.

(2) The heat given off by an equal weight of the same potash reacting upon the weight of pure water contained in the calorimeter.

(3) The heat absorbed by the solution of an equal weight of pure hydroxylamine hydrochloride in the same quantity of water.

(4) The heat given off when the hydroxylamine hydrochloride in a weak solution is decomposed by the diluted potash; in this case the hydroxylamine is set at liberty at first without being destroyed.

All these data being obtained by special experiments, it is easy to calculate the heat given off by the simple destruction of an equivalent of hydroxylamine.

5. The results deduced from the experiments are as follows:—

$3NH_3O$ dissolved = $N_2 + NH_3 + 3H_2O$ disengaged[1] + 57·3 & + 56·7; mean + 57·0 Cal.

Other distinct experiments have given:—

NH_3O diss. + HCl dilute at 24° liberates[2]	+ 9·2
NH_3OHCl cryst. (1 p. of salt + 90 p. of water) in dissolving at 24°	− 3·31
$(NH_3O)_2SO_4H_2$ cryst. + 100 parts of water at 12·5 ...	− 2·90
$(NH_3O)_2$ dilute + H_2SO_4 dilute, at 12·5	+ 10·8

6. Formation from the elements:—

$N + H_3 + O$ = NH_3O dissolved liberates	+ 19·0
$N + H_3 + O + HCl$ dilute = NH_3OHCl diss.	+ 28·2
$N + H_4 + O + Cl$ gaseous = NH_3OHCl cryst.	+ 70·8
$N_2 + H_6 + O_2 + SO_4H_2$ dilute = $(NH_3O)_2H_2SO_4$ diss....	+ 29·8
$N_2 + H_6 + O_6 + S$ = $(NH_3O)_2H_2SO_4$ cryst.	+ 138·8

7. Different modes of formation:—

OXIDATION OF AMMONIA.

NH_3 diss. + O = NH_3O diss. will absorb	− 2·0
NH_3HCl diss. + O = NH_3OHCl diss.	− 7·2
NH_3HCl cryst. + O = NH_3OHCl cryst.	− 5·9

[1] In the calculation of the experiments the formation of a little nitrogen monoxide was taken into account, say 3 to 4 per cent., under the conditions in which I was working.

[2] According to the decomposition of pure hydrochloride dissolved in water, by dilute potash.

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SIMILAR OXIDATION OF THE SULPHATE.

$(NH_3)_2H_2SO_4$ diss. + O = $(NH_3O)_2H_2SO_4$ diss. ... ... − 5·7
$(NH_3)_2H_2SO_4$ cryst. + O = $(NH_3O)_2H_2SO_4$ cryst. ... ... − 4·1

We see that a fixed oxidation would absorb quantities of heat varying from − 2·6 to − 7·2; according to whether it takes place on free hydroxylamine or on its salts in solution. It is essential to note that this quantity is negative, unlike what takes place for oxides of nitrogen.[1] Moreover, the three above-mentioned reactions are purely theoretical; they are, however, worthy of mention, as by their endothermal nature they may be compared to the formation of oxygenated water and to that of nitrogen monoxide.

We get for the formation of hydroxylamine by the hydrogenation of nitric oxide—

$$NO + H_2 + \text{water} = NH_3O \text{ diss.} + 40{\cdot}6.$$

This last reaction is effected, in fact, by means of nascent hydrogen, that is to say, in reactions which furnish, in addition, the heat which would have been given off at the time of the formation of the free hydrogen, under the same conditions.

8. Reactions of hydroxylamine. Action of hydrogen—

$$NH_3O \text{ dissolved} + H_2 = NH_3H_2O \text{ dissolved} + 71{\cdot}0.$$

We see by this that the hydroxylamine will be easily changed into ammonia by the nascent hydrogen. This is why the production of the first body, in the reduction of the oxides of nitrogen, requires very special conditions. Among all the formations of nitric compounds that nitric acid can effect by producing oxidation, that of hydroxylamine gives off the least heat. In fact, each equivalent of oxygen imparted by the dilute nitric acid to the body to be oxidised with the formation of hydroxylamine gives off − 16·4 Cal. less than free oxygen, whereas the free formation of ammonia gives off only − 12·1 Cal. less, that of nitric oxide − 12 Cal., that of nitric peroxide − 9·6 Cal., that of nitrogen − 1·4 Cal., etc.[2]

9. Action of oxygen. Heat of combustion—

$$2NH_3O \text{ dilute} + O = N_2 + 3H_2O \text{ liquid} + 84{\cdot}5.$$

The combustion of dilute ammonia gives off a little less, or + 82·5; but it requires three times as much oxygen for the same weight of nitrogen contained in the compound.

We get—

$2NH_3O$ dilute + O_2 = N_2O gas + $3H_2O$ liquid ... ... + 74·2
$4NH_3O$ „ + O_5 = N_4O_5 dilute + $6H_2O$ liquid ... ... + 65·4
$2NH_3O$ „ + O_4 = N_2O_5 „ + $3H_2O$ „ ... ... + 80·3
$2NH_3O$ „ + O_5 = $2HNO_3$ „ + $2H_2O$ „ ... ... + 98·8

[1] p. 171, nitric oxide; pp. 178 and 179, nitrogen trioxide; p. 189, nitric peroxide.
[2] See p. 200.

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or for each fixed equivalent of oxygen (8 grms.), 37·1, 26·1, 20·1, 19·8.

10. Action of dilute alkalis.

The reaction of the alkalis upon the salts of hydroxylamine is worthy of notice. Dilute alkalis confine themselves to displacing the hydroxylamine, at least in an operation of short duration. The measurement of the heat given off shows that hydroxylamine is a much weaker base than baryta, potash, and even ammonia. In fact, with dilute potash and the hydrochloride it was—

$$2NH_3OHCl \text{ dissolved} + K_2O \text{ dilute at } 23°, + 4{\cdot}44;$$

with dilute baryta and the sulphate at 12·5°—

$$2(NH_3O)H_2SO_4 \text{ dilute} + BaO \text{ dilute}, + 7{\cdot}8;$$

likewise with ammonia and the chloride—

$$NH_3OHCl \text{ dissolved} + NH_3 \text{ dilute at } 12{\cdot}5°, + 3{\cdot}35.$$

These thermal measurements show that the displacement of the hydroxylamine by the ammonia is complete, *i.e.* in proportion to the weight of this base. It is the same even when we employ only half the ammonia necessary for a complete decomposition.

Hydroxylamine is, therefore, one of the weakest of bases, hence its salts offer a very pronounced acid reaction.

It was found that the sulphuric acid, which is combined with it, might be accurately estimated by an alkalimetric test; almost like the soda in borax, but by an opposite test.

11. The *concentrated alkalis* act very differently, for they determine the decomposition of hydroxylamine itself. Thus with *concentrated potash* we get destruction of the hydroxylamine.

12. *Ammonia.* 1. With a saturated aqueous solution of ammonia at about zero, the hydroxylamine is displaced in its salts without undergoing decomposition, even at the end of several days. 2. With ammoniacal gas and solid hydroxylamine hydrochloride there is slow decomposition of the hydroxylamine. Theory indicates that the displacement properly so called—

$$NH_3OHCl \text{ solid} + NH_3 \text{ gas} = NH_4Cl \text{ solid} + NH_3O, \text{ liberates } + 12{\cdot}6 - a,$$

a being the heat of dissolution of NH_3O, a compound which appears to be liquid.

In fact, it was observed that the dry hydrochloride absorbs the ammoniacal gas immediately, in the proportion of one equivalent, and even a little more. If we employ a considerable excess of ammoniacal gas, working over mercury, and immediately remove

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this excess by means of a gas pipette, the gas separated contains barely a few hundredths of a gas almost insoluble in water (nitrogen or nitrogen monoxide), which shows that the decomposition of the hydroxylamine is almost inappreciable under these conditions. However, the gas so separated contains a few hundredths of the vapour of hydroxylamine. We may prove this by the following process. This gas is heated with a few drops of water, which dissolve the vapour at the same time as the ammonia; the gas not dissolved is taken away by means of a gas pipette, then we add to the water a large piece of potash (with its surface previously damped, so as to eliminate the gases adhering to it); under these conditions the hydroxylamine which existed in the water, and consequently in the ammoniacal gas which this water had dissolved, is immediately destroyed with formation of nitrogen, which is really produced and which may then easily be observed.

Hydroxylamine may then be regarded, according to these facts, as existing in a free state and in a liquid form, in the testing apparatus, where it impregnates the ammonium chloride.

Its vapour tension, as deduced from the preceding experiments, would indicate a boiling point near that of water.

But hydroxylamine so formed does not exist long in a state of purity; it is destroyed little by little, giving rise especially to nitrogen monoxide and ammonia—

$$4NH_3O = N_2O + 2NH_3 + 3H_2O.$$

At the end of forty-eight hours, nearly two-thirds had undergone this transformation, as found by an exact analysis made of the products derived from a known weight of the hydrochloride; about a seventh had in the same time changed into nitrogen and ammonia.

The fundamental reaction, which in this case produces nitrogen monoxide, gives off, according to calculation, + 48·4 Cal., a result relating to the following conditions—

$$4NH_3O \text{ dilute} = N_2O \text{ gas} + 2NH_3 \text{ dilute} + 3H_2O \text{ liquid}.$$

The real reaction, NH_3 being supposed to be gaseous, and a being the heat of solution of NH_3O, gives off $+ 39{\cdot}6 - a$.

We see that all these quantities are far below the heat given off in the reaction engendered by nitrogen, viz. + 57. This explains why this last reaction preponderates under the influence of concentrated potash.

13. From these facts it follows that hydroxylamine is only stable in presence of acids, but its union with these agents deprives it of part of its energy. This is, moreover, generally the case in chemistry; a system is the more stable, all else being equal, in proportion as the fraction of its energy which it loses is greater (see p. 123).

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In the same way, it was found that hydrochloric acid gas in excess, and also boron fluoride, do not determine the decomposition of hydroxylamine, notwithstanding their avidity for the water which might be formed at its expense. But this relative stability is explained by the preceding considerations, *i.e.* in proportion to the formation of the saline compounds.

But on the contrary, hydroxylamine, when free or dissolved in a very small quantity of water, *i.e.* possessed of all its energy, manifests a strong tendency to spontaneous destruction, and this destruction works in a way that gives off the more heat the more suddenly it is effected.

14. To recapitulate these *various processes of decomposition*.

(1) In the most simple decomposition

$$NH_3O \text{ dissolved} = N + H + H_2O + \text{water would liberate} + 50{\cdot}0.$$

But this sudden reaction has not been observed; the nascent hydrogen remained completely associated with the nitrogen in these conditions, and it forms ammonia, a formation accompanied by a second liberation of heat.

(2) In a sudden reaction we see the transformation of a third of the nitrogen into ammonia, as follows—

$$3NH_3O \text{ dilute} = NH_3 \text{ dilute} + 2N + 3H_2O,$$

a reaction which gives off in addition + 7, or altogether + 57.

We observe also the absence of the compound NH, which one would think ought to appear under these conditions. Though sought for particularly, no trace of it was obtained.

The formation of water itself, which it would seem *à priori* ought to be effected in preference, preponderates only in the sudden reaction brought about by potash; probably by reason of the tendency of this alkali to form hydrates with liberation of heat. Thus the slightest influence determines the manner in which this unstable compound is destroyed.

(3) On the contrary, in the spontaneous decomposition of hydroxylamine, such as takes place in the presence of ammoniacal gas, we see chiefly nitrogen monoxide appear, with less liberation of heat ($+ 48{\cdot}4 \times 2$ instead of $+ 57 \times 2$, all the substances being supposed to be in solution).

15. *Constitution.* This last decomposition, effected upon two molecules of hydroxylamine, one of which abstracts the hydrogen from the other, recalls the resolution of an aldehyde into the corresponding alcohol (or rather carburet) and acid. We may here remark that the *slow decomposition* of hydroxylamine *is at the same time that which develops least heat and which is produced in preference*, under conditions in which most care is taken. Moreover, it takes place *at exactly the same temperature* as the decomposition that gives off the most heat. But these

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various relations are not necessary, and we might quote contrary examples *in which a slow decomposition gives off more heat than a rapid one effected at the same temperature* (decomposition of barium dioxide by a diluted acid, with the rapid formation of oxygenated water, which is itself slowly resolved into water and free oxygen; the decomposition of a hypochlorite by a dilute acid, &c.).

The initial temperature of the reactions is not connected except in a general manner with their unequal thermal value, as is shown by the comparison of the reactions of potassium chlorate and iodate. In short, the conditions of more or less rapid action or higher or lower initial temperature are not those that regulate the phenomena.

On the contrary, *the phenomena are determined, on the one hand, by the general tendency towards the conservation of the initial molecular condition, and, on the other hand, by the tendency of any system towards the condition that corresponds to the maximum of heat given off.* This last condition is realised fully whenever the corresponding bodies can begin to be produced in the conditions of the experiments. It is in order to avoid, so far as possible, the realisation of conditions favourable to the production of these bodies that we avoid raising the temperature and hurrying the reactions. We thus keep as closely as possible to the primitive molecular type.

Without dwelling longer on considerations of this order, it may be said in conclusion that the thermal observations confirm and specify the unstable properties of hydroxylamine, and this instability is due to the exothermal character of its various decompositions.

§ 5. Heat of Formation of some Organic Alkalis.

First Section—General Remarks.

1. Ammonia, on uniting with organic compounds, such as hydrocarbons, alcohols, aldehydes, acids, forms compounds of various natures, alkalis and amides in particular.[1]

The thermal study of these compounds has been very little worked. It would be of great interest in the study of the force of explosive substances derived from ammoniacal salts, cyanides, diazo compounds, etc. The author measured the heat of formation of the cyanide compounds, of several diazo compounds, and of some alkalis and amides. As special chapters are devoted to the cyanide series and the diazo compounds, the alkalis and amides will only be discussed here.

[1] "Traité Élémentaire de Chimie Organique," tom. xi. pp. 224 and 313. Second edition (1881), with the collaboration of M. Jungfleisch, published by Dunod.

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Second Section—Ethylamine.

1. This alkali is gaseous in summer; it boils at + 18·1, it is extremely soluble in water, and forms well-defined salts.

2. *Analysis.* Its purity was proved by eudiometric analysis, a more reliable process than analysis by weight for such compounds. These are the results in volume :—

ETHYLAMINE.

Volume of the Gas.	CO_2 produced.	Nitrogen.	Total diminution after combustion and absorption of CO_2.
Found 100	201	50·5	428
Calculated 100	200	50·0	425

3. *Heat of combustion of ethylamine.* Four detonations made with weights of this base ranging between ·11 and ·12 of a grm. gave, at about 20·5° with gaseous ethylamine (C_2H_7N = 45 grms.), the volume being constant—

$$2C_2H_7N \text{ gas} + O_{15} = 4CO_2 \text{ gas} + 7H_2O \text{ liquid} + N_2.$$

According to the initial weight of the alkali.	According to the final weight of the carbonic acid.
416·3 Cal.	413·0 Cal.
409·3 „	403·3 „
400·7 „	406·4 „
402·7 „	416·4 „
Mean 407·2 „	Mean 409·3 „

The general mean + 408·5 must be increased by 1·2 to pass to the ordinary heat of combustion under constant pressure, which makes + 409·7 Cal. This number entails a limit of error of about ± 4 Cal., an uncertainty that also occurs in the following deductions.

4. *Heat of formation.* The heat of combustion of the elements being + 429·5, we get for the heat of formation—

From the elements—
C_2 (diamond) + H_7 + N = C_2H_7N gas ... ... + 19·8
C_2 (charcoal) „ „ ... .. + 25·8
From ammonia—
C_2 (diamond) + H_4 + NH_3 = C_2H_7N gas ... ... + 7·6
C_2 (charcoal) „ „ ... ... + 13·6
From ethylene—
$C_2H_4 + NH_3 = C_2H_7N$ ... ... + 23·0
From alcohol—
$C_2H_5(HO)$ gas + NH_3 gas = $C_2H_7N + H_2O$ ... ... + 6·1

5. *Solution in water.* Two experiments made at 190° on

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weights of gaseous ethylamine, equal respectively to 2·555 grms. and 2·415 grms., and dissolved in 400 grms. of water, gave for C_2H_7N (45 grms.); + 12·92 and + 12·90; mean 12·91 Cal. These results exceed those of ammonia by one-half.

6. *Formation of salts in solution at* 190°.

C_2H_7N	(1 eq. = 7 litres)	+ HCl	(1 eq. = 2 litres)	liberates	+ 13·2
„	„	+ $C_2H_4O_2$	„	„	+ 12·9
„	„	+ H_2SO_4	„	„	+ 15·2

figures that are intermediate between those given by potash and ammonia.

Third Section.—Trimethylamine.

1. This is a liquid that boils at 9°; it is consequently gaseous at the ordinary temperature. It is very soluble in water and forms well-defined salts.

2. *Analysis.* These are the results obtained by eudiometric analysis:—

TRIMETHYLAMINE.

Volume of the Gas.	CO_2 produced.	Nitrogen.	Total diminution after combustion and absorption of CO_2.
Found 100	302	50	589
Calculated 100	300	50	575

3. *Heat of combustion of trimethylamine.* Three detonations made with weights of the base ranging between ·112 grms. and ·186 grms. gave for C_3H_9N (59 grms.), the volume being constant—

$$2C_3H_9N + O_{21} = 6CO_2 \text{ gas} + 9H_2O \text{ liquid} + N_2.$$

According to the initial weight 586·2, 583·5, 601·1; mean + 590·3.

According to the final weight of the carbonic acid, on an average + 591·7.

The general mean is + 590·5, which gives for the heat of combustion at a constant pressure + 592, with a limit of error of about + 6 Cal., an uncertainty that applies to the following deductions.

4. *Heat of formation.*

From the elements—			
C_3 (diamond) + H_9 + N = C_3H_9N gas	...	...	− 9·5
C_3 (charcoal) „ „	...	...	− 0·5
From ammonia—			
C_3 (diamond) + H_6 + NH_3 = C_3H_9N gas	...	...	+ 2·7
C_3 (charcoal) „ „	...	...	+ 6·3
From methylic alcohol—			
$3[CH_3(HO)] + NH_3 = (CH_3)_3NH_3 + 3H_2O$ gas	...		− 7·3 × 3

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The exact deductions that can be drawn from the heats of combustion are really only valid for low heats of combustion or for considerable differences, and attention must be called to the limits of error involved in calculations of this kind, in order to prevent any misapprehensions.

5. *Solution in water.* Three experiments, made at about 20°, on weights of the base equal respectively to 4·753, 4·994, and 4·633 grms., and dissolved separately in 400 grms. of water, gave for C_3H_9N (59 grms.) gaseous + 270 H_2O about + 12·82, + 12·76, + 13·2; on an average + 12·90 Cal.

This figure is equal to the heat of solution of ethylamine, and it shows in both bases a special affinity for water.

6. *Dilution.* This affinity may be shown still more clearly as regards trimethylamine, by experiments on dilution.

A liquid saturated at about 19° contained 409·6 grms. of the base per litre, or 478 grms. per kilog. Its density was ·858 at 16°. It corresponded to $C_3H_9N + 7{\cdot}17H_2O$.

On being diluted with thirty times its volume of water, it gave off + 3·89 Cal. at 19°.

Thus C_3H_9N, on combining with $7{\cdot}17H_2O$, gives off only + 9 Cal., and that its subsequent dilution gives off about half as much heat.

For purposes of comparison we may repeat here some of the figures obtained with ammonia.

$NH_3 + 7H_2O$, by its subsequent dilution, gives off + ·32.
$NH_3 + 19H_2O$, gives off only + ·02.

These figures show that ammonia has much less tendency than trimethylamine to form hydrates.

The heat of dilution of the latter base when concentrated is very considerable, and its value amounts to even double that of potash and soda, taken at a corresponding degree of concentration. The heat of dilution of concentrated trimethylamine is quite comparable to that of the hydracids. Now, such values express the formation of certain successive hydrates,[1] a very important circumstance in the study of the reactions of hydracids, as well as those of trimethylamine.

7. *Formation of salts in solution.* At 21° it was found—

C_3H_9N (1 eq. = 5 litres)	+ HCl (1 eq. = 2 litres)	...	+	8·9
„ „	+ $C_2H_4O_2$	„ ...	+	8·3
„ „	+ H_2SO_4	„ ...	+	10·9

As a check to these results, we get by a double reciprocal decomposition—

C_3H_9N (1 eq. = 2 litres) + KCl (1 eq. = 2 litres) + 4·40
K_2O (1 eq. = 2 litres) + C_3H_9NHCl (1 eq. = 2 litres) − 0·28 } $M' - M = + 4{\cdot}7$

[1] "Essai de Mécanique Chimique," tom. ii. pp. 151, 167.

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From these data it follows that the heat given off by the union of potash with hydrochloric acid exceeds by + 4·7 that given off by trimethylamine (p. 118), which gives for the combination of this base in solution with dilute hydrochloric acid, the value + 9, which results agree with that given above.

We also see, by the above numerical experiments, that the potash entirely, or almost entirely, displaces the trimethylamine in its acid compounds. It seems, however, that there are some indications of division—

$$\left.\begin{array}{l} C_3H_9N \text{ (1 eq. = 2 litres)} + NH_3HCl \text{ (1 eq. = 2 litres)} - 2{\cdot}33 \\ NH_3 \text{ (1 eq. = 2 litres)} + C_3H_9NHCl \text{ (1 eq. = 2 litres)} + 1{\cdot}17 \end{array}\right\} M - M' = + 3{\cdot}5$$

The division of the acid between the two bases is here evident. It is no doubt due to the formation of dissolved hydrates of trimethylamine as mentioned above, and also of its hydrate, which is discussed further on. Without entering further into this point, we will content ourselves with saying that we deduce from these figures, for the heat of neutralisation of trimethylamine by hydrochloric acid, + 8·95.

The three values found agree, viz. 8·9, 9, 8·95. They are lower by about a third than the heats of neutralisation of potash by the corresponding acids; they are even lower than the results obtained with ammonia. Their numerical values approximate, on the contrary, to the heats of neutralisation of the same acids by hydroxylamine and by aniline, bases which are much weaker than ammonia.

Again, we find—

C_3H_9N (1 eq. = 8 litres) + CO_2 (44 grms. in 26 litres) liberates + 4·4
C_3H_9NHCl (1 eq. = 2 litres) + Na_2CO_3 (1 eq. = 2 litres) „ − 1·17

The last value indicates the transformation of trimethylamine chloride into sodium chloride, the strong base, *i.e.* the soda, taking the strong acid, *i.e.* the hydrochloric acid, as it happens also between ammonium chloride and sodium chloride, and for the same reasons.[1] If we suppose the reaction to be total, we deduce from it that CO_2 in solution, + C_3H_9N in solution, would give off + 4·1 in the presence of 4 litres of water.

In the presence of 17 litres of water the experiment gave a lower value, which seems to indicate the gradual dissociation of the carbonate by dilution, always as with ammonia.[2]

8. *Trimethylamine hydrochloride.* The heat of formation of this salt has already been given in a state of solution. In order to estimate it in a solid state the heat of solution was determined upon a fine specimen, supplied by M. Vincent, carefully dried upon blotting paper, under a bell glass over sulphuric acid.

[1] For discussions of reactions of this order, see "Essai de Mécanique Chimique," tom. ii. pp. 712 and 717.

[2] "Annales de Chimie et de Physique," 4e série, tom. xxxix. pp. 477–485.

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The analysis of it agreed pretty closely with the formula—

$$C_3H_9NHCl$$

10 grms. of this salt were dissolved in 500 grms. of water at 180°.

A slight absorption of heat was produced, answering to −·5 Cal., for

$$C_3H_9NHCL = 95{\cdot}5 \text{ grms.}$$

According to this result,

C_3H_9NC gas + HCl gas = C_3H_9NHCl solid liberates + 39·8 Cal.

This value is lower than the heat of formation of solid ammonium chloride starting from its gaseous components, or + 45·5 Cal.

But the value deduced probably does not represent the actual heat of formation of trimethylamine chloride as it exists in diluted solutions. In fact, this salt attracts the atmospheric moisture with such avidity that it falls almost immediately into a liquid state, which indicates the formation of a definite hydrate in its solutions, whereas ammonium chloride seems to exist in its solutions in an anhydrous state. The heat of formation of anhydrous trimethylamine chloride must therefore be increased in its solutions by the heat of formation of its hydrate, if we wish to calculate the energy really called into action in the formation of the chloride in solution, *i.e.* the true energy put forth in the reactions of this substance.[1]

§ 6. The Heat of Formation of some Amides.

1. The amides are derived, in general, from the union of the acids and ammonia, with separation of water, that is, they are ammoniacal salts deprived of the elements of water. This class comprises a number of very important compounds; it extends even as far as the albumenoid principles which form the basis of animal tissues and organs. Many explosive substances are also included in it. But their thermal study is not as yet far advanced, with the exception of that of the cyanide series, which will be discussed in a subsequent chapter. Besides these, the author has only, up to the present, examined two amides, viz. oxamide and formamide.

2. *Oxamide.* Oxamide is a solid body, almost insoluble, differing from ammonium oxalate by the elements of water—

$$C_2H_2O_4(NH_3)_2 = C_2H_4N_2O_2 + 2H_2O.$$

It may be obtained, either by the decomposition of the salt,

[1] We must also take into account its own state of dissociation as a hydrate and as an anhydrous salt. "Essai de Mécanique Chimique," tom. ii. p. 445.

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or by the reaction of ammonia upon oxalic ether, a reaction more accessible to measurement.

$$\left.\begin{matrix}C_2H_4\\C_2H_4\end{matrix}\right\}C_2H_2O_4 + 2NH_3 = C_2H_4N_2O_2 + 2C_2H_6O_2.$$

In fact, the reaction of ammonia upon oxalic ether is immediate. This circumstance was taken advantage of to determine the heat of formation of oxamide. For example, 1·9495 grm. of oxalic ether and 10 cms. of a very concentrated solution of ammonia were enclosed in a phial,

$$(NH_3 3H_2O \text{ about}),$$

the two bodies being brought together in a little receiver immersed in the water of the calorimeter. The reaction is complete at the end of three or four minutes. The products are then mixed with the water of the calorimeter, so as to bring the whole into a state of dilute aqueous solution.

All the calculations being made,[1]

$$(C_2H_4)_2C_2H_2O_4 \text{ pure} + 2NH_3 \text{ dilute} = C_2H_4N_2O_2 \text{ solid} + 2C_2H_6O \text{ dilute}$$

gave off + 26·2 and + 26·6, on an average + 26·4, or 13·2 × 2.

Now the formation of ammonium oxalate, by means of oxalic ether and ammonia, in the presence of a large quantity of water—

$$(C_2H_4)_2C_2H_2O_4 \text{ pure} + 2NH_3 \text{ dilute} = C_2H_2O_4 2NH_3 \text{ dissolved} + 2C_2H_6O \text{ dilute},$$

would give off + 16·0 × 2.

By subtracting from the difference (16·0 − 13·2) × 2, the heat of solution of the ammonium oxalate, or − 4 × 2, we find that the formation of oxamide from the solid salt,

$$C_2H_2O_4 2NH_3 \text{ cryst.} = C_2H_4N_2O_2 + 2H_2O \text{ liquid, absorbs } - 2{\cdot}4 \text{ or } - 1{\cdot}2 \times 2.$$

In the conditions of direct metamorphosis, by the action of heat on ammomium oxalate, the water takes a gaseous form. Hence

$$C_2H_2O_4 2NH_3 \text{ cryst.} = C_2H_4N_2O + 2H_2O_2 \text{ gas absorbs } - 21{\cdot}7 \text{ or } - 10{\cdot}8 \times 2.$$

From the above measurements we deduce the heat of formation of oxamide from the elements

$$C_2 \text{ (diamond)} + H_4 + N_2 + O_2 \ldots . + 140{\cdot}0.$$

3. *Formamide.* It was found that the transformation of formic amide into formic acid and ammonia (or rather into

[1] The author also studied the action of dilute ammonia upon oxalic ether, dissolved beforehand in a large quantity of water. This reaction gave off + 8·2 × 2. It did not produce oxamide, all the bodies remaining in solution, even after several days, no doubt in the form of oxamic ether.

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ammonium chloride) is effected by means of concentrated hydrochloric acid.

According to the figures obtained, the reaction CH_3NO diss. $+ H_2O = CH_2O_2NH_3$ in solution, gives off + 1·0.

The opposite reaction, the two conditions being similarly comparable, absorbs − 1, a result very near − 1·2 observed with oxamide. It is also very near the absorption of heat produced in the formation of ethers.

Reciprocally, the fixing of the water on the oxamide (as upon formamide) with the production of ammoniacal salts, gives off in heat + 2·4 for oxamide, always like the fixing of water on the ethers.

4. *We see by this that the hydration of organic compounds generally gives off heat*, whether we are considering the decomposition of ethers dissolved in acids and dilute alcohols, the transformation of amides into ammoniacal salts, the transformation of anhydrous acids into hydrated acids, or of the acid chlorides into hydrochloric acid and dilute organic acids. This is a very general result, to which attention was drawn in 1865, and which is confirmed and put in a definite form by the present experiments. Its importance in the theory of animal heat may be easily understood. From a more technical point of view, this relation, and especially the values found for the hydration of oxamide and formamide, may be useful in the approximate calculation of the heat of formation of amidated compounds capable of being employed in the manufacture of explosive substances.

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CHAPTER VII.

HEAT OF FORMATION OF NITROGEN SULPHIDE.[1]

§ 1. Nitrogen Sulphide.

1. This body is a solid, crystallised, yellow, explosive substance, expressed by the formula NS, and by the equivalent 46. It is prepared by the action of ammoniacal gas upon sulphur chloride, dissolved in carbon disulphide.[2]

The specimen used in these experiments gave upon analysis—

	Found.	Calculated.
N	69·64	69·56
S	30·41	30·44
H	0·01	—

2. Nitrogen sulphide is stable at the ordinary temperature. It is preserved without alteration both in dry and in damp air. It may be moistened and then dried at 50° without any appreciable alteration, even should these operations be repeated several times.

Its density at 15° was found to be equal to 2·22.

Nitrogen sulphide detonates with violence upon being struck with a hammer, but its sensitiveness to this shock is less than that of mercury fulminate.

On being heated it explodes at 207° and above this heat. Its decomposition is, however, much slower than that of mercury fulminate or diazobenzol nitrate. We may remark that this temperature of conflagration is near that of the combustion of sulphur freely exposed to air.

3. *Heat of detonation.* The decomposition of the nitrogen sulphide was provoked in a pure dry atmosphere of nitrogen, in a bomb lined with platinum.

It was ignited by means of a very fine metallic wire, plunged nto the substance and heated to incandescence by means of an

[1] This study was made jointly with M. Vieille.

[2] Fordoz et Gélis, "Annales de Chimie et de Physique," 3° série, tom. xxxii. p. 385.

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electric current. Two experiments gave, the volume being constant—

Weight of the substance.	Heat given off per grm.	Per equivalent (46 grms.).
2·997 grms. ...	... 701·1 ...	...} + 32·2 Cal.
2·979 „ ...	... 700·4 ...	...}
	Mean 700·7	

At a constant pressure, we should have had + 31·9. The experiment gave for 1 grm. 243·1 cms. of gas (the volume being reduced to 0° and ·76 metre).[1]

Theory gives 242·2 cub. cms.

These gases consisted of pure nitrogen, within about $\frac{1}{250}$th. Thus the decomposition was produced according to the equation NS = N + S, *i.e.* the nitrogen sulphide is resolved purely and simply into its elements.

4. *Heat of formation.* From these results we conclude that the formation of nitrogen sulphide from its elements,

$$N + S = NS, \text{ absorbs } - 32{\cdot}2 \text{ Cal.},$$

the volume being constant, or 31·9 Cal. at a constant pressure.

This formation is, therefore, endothermal, which explains why it does not take place directly. But it is effected by making ammoniacal gas act upon sulphur chloride. The chlorine in this latter compound unites with the hydrogen of the ammonia to form hydrochloric acid, and consequently ammonium chloride, while the nitrogen sulphide is forming. This transformation finally gives off + 123·0 Cal. The energy consumed in the association of the sulphur and the nitrogen (− 31·9) is thus furnished by the formation of the hydrochloric acid, or rather by that of the ammonium chloride, at the expense of the sulphur chloride and the ammoniacal gas (+ 230·1 − 75·2).

5. It will be observed that the combination of the nitrogen with the sulphur absorbs heat (− 31·1 Cal.), exactly like the combination of nitrogen with oxygen (− 21·6 Cal.). The nitrogen sulphide is, therefore, analogous to nitric oxide as regards its endothermal character, as well as its formula. This is a fresh proof of the general analogy existing between the conditions of formation of oxygenated compounds and those of sulphuretted compounds. It is difficult to carry further these points of resemblance in the heats of formation, seeing that the conditions of the two compounds are not comparable, any more than the conditions of the elements, although a certain compensation may be allowed between the solid form of the sulphur and that of nitrogen sulphide.

6. *Heat of combustion.* If we are working in air or in oxygen, nitrogen sulphide burns—

$$NS + O_2 = N + SO_2,$$

and gives off + 101·1 at a constant pressure.

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§ 2. Nitrogen Selenide.

1. This compound is similar to nitrogen sulphide; it has recently been the subject of careful study on the part of M. Verneuil,[1] who has fixed its formula at NSe. He kindly furnished M. Vieille and the author with a specimen for the experiments which they were making upon explosive substances.

It is an amorphous powder, of a deep orange colour, very dangerous to handle. It explodes at about 230°, according to M. Verneuil. It also explodes either by friction or by a very slight percussion of iron upon iron, or a more violent percussion of wood upon iron. The contact of a drop of sulphuric acid also makes it explode.

2. *Heat of detonation.* We effected the explosion in our usual apparatus by the same process as we adopted for nitrogen sulphide. Working with 3 grms. of the substance, two trials gave, for the reaction—

$$NSe\ (93\ grms.) = N + Se$$

+ 42·9 Cal. and + 42·4 Cal., on an average + 42·6 Cal. with a constant volume, or + 42·3 Cal. at constant pressure, a value which is only approximate, owing to the difficulty of obtaining this substance quite pure.

3. *Heat of formation.* We conclude from these observations that the nitrogen selenide is formed from its elements, with an absorption of heat equal to − 42·3 Cal. at a constant pressure.

4. *The heat of combustion.*

$$NSe + O_2 = N + SeO_2$$

is equal to + 99·9 Cal.

5. Thus nitrogen selenide is an endothermal combination (− 42·3). It may, therefore, in this respect be classed with nitrogen oxide (− 21·6 Cal.) and nitrogen sulphide (− 31·9 Cal.), the condition of these bodies being almost comparable as regards the nitrogen sulphide and selenide, and the heats absorbed forming a sort of arithmetical progression at the rate of about 10·5. In all cases they increase in absolute value with the equivalent, in accordance with a relation that is pretty general among the series of similar compounds,[2] such as the series of chlorine, bromine, and iodine; the series of nitrogen, sulphur, and selenium, etc. It follows that in such series the explosive character of the endothermal compounds becomes more and more pronounced in proportion as their atomic weight is greater.

[1] "Bulletin de la Société Chimique," 2e série, tom. xxxviii. p. 548.
[2] "Annales de Chimie et de Physique," 5e série, tom. xxxii. p. 391.

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CHAPTER VIII.

HEAT OF FORMATION OF COMPOUNDS DERIVED BY THE ACTION OF NITRIC ACID UPON ORGANIC SUBSTANCES.

§ 1. General Remarks.

1. A large number of artificial compounds result from the association of organic principles with nitric acid. These compounds are generally explosive, and they play an important part both in warfare and in mining industry. In order to estimate their explosive force, it is necessary to know the heat disengaged in their decomposition. In fact, the explosive force of nitro-carbon compounds results from a kind of internal combustion analogous to that of ordinary gunpowder, from which, however, it is distinguished by the fact that the nitric acid and combustible principle are intimately combined, instead of being simply mixed together, as in the case of ordinary gunpowder. This force is greater in proportion as the combustion develops more gas and more heat. Now, if all else be equal, the heat disengaged by the combustion will be inversely proportional to that disengaged by the previous union of the nitric acid with the organic principle.

2. The heat disengaged in the formation of the following more important nitrated compounds by means of nitric acid was determined—nitric ether, nitroglycerin, nitro-mannite, gun-cotton, nitro-cellulose or xyloidin, the nitro, dinitro, and chloro-nitrobenzene, and nitrobenzoic acid. The heat of formation of trinitrophenol, otherwise called picric acid, and of its salts, was deduced from calculations based on certain analogies which have just been confirmed by some experimental determinations of Sarrau and Vieille. In 1871 Troost and Hautefeuille had published, a few days after the author's communication, some measurements relating to the heat of formation of various nitrated derivatives, the results agreeing very closely.

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3. We may, then, arrive at the heat disengaged in the formation of nitrated compounds from pure nitric acid and organic principles, such as alcohol, benzene, phenol, glycerin, mannite, cellulose, etc. But this quantity does not enable us to calculate the heat given off by their explosive decomposition, even if we know exactly the products of this decomposition. It is necessary, in addition, to have the heat of formation of these products from their elements, together with that of nitric acid, water, and the original compound that gave rise to the nitrated body.

The products of the explosive decomposition of nitrated compounds are generally simple, *e.g.* water, carbonic acid, and nitrogen; these three being the only substances produced in a complete combustion, such as that of nitroglycerin or nitromannite. But in incomplete combustion, where the oxygen is deficient, as in that of gun-cotton, we get also carbonic oxide, hydrocyanic acid, hydrogen, marsh gas, occasionally oxides of nitrogen, etc. The heat of formation of all these substances should be known beforehand.

In fact, the heat of formation of all these compounds has already been given (pp. 128, *et seq.*), together with that of nitric acid from its elements. With regard to the original generator of the nitrogenous body, its heat of formation may be determined by its total combustion in oxygen, or by various other processes. For all the substances enumerated above, the heat of formation will be found in the thermo-chemical tables (pp. 136, 137). We will give an example, in order to make this clear. Let us estimate the heat disengaged in the combination of the elements of nitric ether. For this purpose we add the heat disengaged in the formation of alcohol, C_2H_6O (+ 70 Cal.), to that disengaged in the formation of nitric acid, HNO_3 + 41·6 Cal., and then to the sum we add that disengaged in the reciprocal reaction of these two bodies (+ 6·2 Cal.), which reaction produces nitric ether. The sum of these three quantities, minus the heat of formation of the water eliminated in the reaction (H_2O), *i.e.* 69 Cal., gives the quantity, + 49·3 Cal., which represents the heat disengaged by the combination of the elements of nitric ether. On subtracting this quantity from the heat disengaged by the pure and simple combustion of the said elements by means of free oxygen, we get the heat of total combustion of nitric ether in free oxygen, or + 311·2 Cal.

4. In this way were calculated both the *heat of formation from the elements, and the heat of total combustion*, of nitric ether, nitroglycerin, gun-cotton, and nitrobenzene.

The heat liberated by their explosive decomposition can be at once deduced, provided that we know exactly the real equation representing this decomposition. It is also necessary to take into account, in the calculations, the conditions of the decom-

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position; for the figures are not the same when we are working at constant pressure, as in the open air, as when we are working at constant volume, as in a bomb shell or other closed vessel. The rule for determining *corrections* of this nature has already been given (p. 15).

5. Conversely, if we know the heat disengaged by the decomposition of an explosive substance, in a closed vessel, as well as the exact nature of the products, it is easy to deduce the heat of formation of the nitrated compound from its elements. Sarrau and Vieille have followed this method. It furnishes us with a check on the results obtained by the direct method, as the two series of data should at least agree within the limits of error allowed in experiments of this kind.

6. Sometimes the products of the decomposition are either not well known, or are too complicated, or imperfectly defined as to their physical condition—as in the case in which are formed carbonaceous substances still retaining nitrogen, hydrogen, oxygen, etc. This is what happens, for instance, with diazobenzene nitrate and with the picrates.

In cases of this kind, the heat developed by the explosion is always a useful quantity to measure, but it cannot be calculated *à priori*.

7. For a great number of applications it is necessary to measure the heat of formation of such explosive compounds from their elements. We then have recourse to a general method, which consists in causing the body to explode in an atmosphere of pure oxygen. This converts it entirely into water, nitrogen, and carbonic acid. Calculation then becomes easy. This method was employed for diazobenzene nitrate; Sarrau and Vieille also adopted it for the picrates.

8. Instead of oxidising the body by free oxygen, we may do so by means of an oxidising compound. This is frequently done in practice, such as when gun-cotton or the picrates are mixed with potassium nitrate, ammonium nitrate, potassium chlorate, or even sometimes certain metallic oxides.

Under these circumstances it is convenient to calculate the heat of combustion of the hydrocarbon compound, taking into account the heat of formation of the oxidising body, according to the table on page 134.

The calculation is easy if the oxidising substance be potassium chlorate, each equivalent of oxygen supplied entailing a supplementary disengagement of 1·83 Cal.

With ammonium nitrate, the additional energy is enormous, amounting to + 25·05 Cal. per equivalent of oxygen.

With potassium nitrate the calculation is somewhat more complicated, on account of the alkali present, which may change into carbonate or sulphate, according to circumstances. Let us take, for example, a compound containing carbon in sufficient

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quantity to convert all the potash into potassium carbonate. The five equivalents of oxygen supplied by the potassium nitrate will give off, then, 27 Cal. less than if they were free, and generated with the carbon, free carbonic acid; or 5·4 Cal. for each equivalent of oxygen. We may even add that this estimate is not quite exact whenever cooling takes place in an atmosphere of carbonic acid and aqueous vapour, because these convert the neutral carbonate, K_2O, CO_2, into the bicarbonate; K_2O, H_2O, $2CO_2$, causing a complementary disengagement of 248 Cal. (beginning from liquid water). Consequently, the excess of heat developed during the combustion of a hydrocarbon compound, in free oxygen, over that developed by the same combustion by means of potassium nitrate, is reduced to 14·6 Cal. only for KNO_3 (= 101 grms.), *i.e.* to 2·9 Cal. for each equivalent of oxygen employed.

9. We will add that, in cases where the combustion of the explosive body is rendered complete by the addition of an oxidising agent, we must not forget that the weight of the latter is added to that of the explosive substance; so that a gramme of the mixture, subjected to total combustion, may give off less heat than a gramme of the explosive body decomposing separately in pursuance of a less complete oxidation. Various compensations may be made with respect to this. For instance, when it is required to make up one kilogramme of an explosive mixture, copper oxide is the most efficacious of the oxides in use, on account of the smallness of its equivalent (79·2 grms.) and the comparatively low value (38·4 Cal.) of its heat of formation. Lead oxide presents the double inconvenience of an equivalent three times as high (223 grms.) and a greater heat of formation (51·0 Cal.), which diminishes in a corresponding degree the heat given off in combustion in which it is the agent.

The oxides of mercury and silver present, on the contrary, smaller heats of formation (31·0 Cal. and 7·0 Cal.). But the thermal increase resulting from this is counterbalanced with the unit of weight, by the magnitude of their equivalents (216 grms. and 232 grms.).

The oxides of tin and antimony, which are, for a given weight, somewhat richer in oxygen than copper oxide, have heats of formation that are, for each equivalent of oxygen, almost double that of the latter.

It has been thought advisable to give these numbers, because they render definite and correct many of the current ideas on combustion by means of metallic oxides. We see that preference should be given to copper oxide on account of the smallness of its equivalent If lead oxide. and particularly the oxides of mercury and silver, seem to be more powerful, it is no doubt because they react and decompose at a lower temperature; a

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circumstance which enables the reaction to commence and continue with greater vigour. Thus the explosives which they form act with greater violence. But their useful effects, as regards both work and pressure, are much less, even in the case of silver oxide, which is so easily decomposed, and of mercuric oxide, which, on the other hand, furnishes a gaseous metal.

10. We will conclude with one remark. When the explosive substance is an acid, such as picric acid, its salts, already existing as such, will produce a less useful effect than simple mixtures of picric acid and metallic oxide; for their formation involves, at the moment of the union of the acid with the oxide, a liberation of heat, *i.e.* a loss of energy. But, on the other hand, simple mixtures will be more dangerous, less stable, and also subject to spontaneous explosions, owing to the possible combination of the acid with the metallic oxide.

11. We have just calculated the heat of formation of a nitrated derivative, supposing that of the generator to be known. Conversely, if we know the heat of formation of a nitrogenous body from its elements, together with that of nitric acid and water, and also the heat disengaged in the reaction of the nitric acid on the original generator of the nitrogenous body, the heat of formation of this original generator can itself be calculated. We may observe that this method is less direct than the immediate combustion of the last compound; therefore the results are less exact. They are, however, useful as checks.

12. Such are the general conclusions that can be deduced from the measurement of the heat disengaged by the combination of nitric acid with organic compounds. These having been given, the experiments of the author, dating from 1871, will now be described.

First of all, it will be remembered that the action of nitric acid on organic substances gives rise to compounds of two distinct kinds, formed according to a similar equation and with a similar separation of the elements of water; the one kind consists of true *ethers*, capable of being decomposed by alkalis with regeneration of nitric acid and alcohol, whereas the other kind, designated specially by the name of *nitro-compounds*, can no longer be split up by distinct reactions, so as to reproduce the generating substances, which are, in the most simple cases, nitric acid and a hydrocarbon. The cause for this difference of reactions will be explained later on. The ethers themselves are divided into two groups, according to whether they are formed from true alcohols, simple in their function, or from alcohols of mixed function, such as cellulose, or condensed ether, derived from several molecules of glucose, which is itself an aldehydic alcohol.

The heat of formation of several bodies belonging to these

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three groups was measured and found to differ according to the diversity of functions of the bodies experimented on.

§ 2. Nitro-compounds in General.

Nitro-compounds result from the action of nitric acid upon organic substances, with separation of water. For instance, $C_6H_6 + HNO_3 - H_2O$; one, two, three, or four equivalents of nitric acid may thus enter into combination with either a hydrocarbon, an acid, an alcohol, an alkali, etc. Compounds of this class are formed principally in the aromatic series, *i.e.* in the series of compounds derived from benzene, or rather, condensed acetylene. Up to the present the terms of this series are the only ones which have been employed in connection with explosive substances; they are also the only ones that have been studied by the author.

It will be recollected that when nitro-compounds are treated with alkalis, they do not reproduce nitric acid, but various bodies of a special character, and nitrogenous, like the generators themselves. Treated with reducing agents, nitro-compounds do not reproduce the original body, but an amide.

1. *Nitrobenzene*, $C_6H_5NO_2$.

1. The reaction for the production of this compound is as follows:—$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O$.

This was performed in a little platinum cylinder, floating in a platinum calorimeter containg 500 grms. of water. The same conditions were observed as in the calorimetric experiments. The density of the acid used was 1·5, and its composition corresponded to the formula, $HNO_3 + \cdot 335H_2O$.

Fifteen grms. of this acid were poured into the little platinum cylinder, which was then closed with a cork coated with paraffin. The temperature of the water in the calorimeter was taken by means of a thermometer sensitive to $\frac{1}{200}$ of a degree; and the temperature of the nitric acid with a smaller thermometer sensitive to $\frac{1}{20}$ of a degree.

The two temperatures being made to agree, the cork was then removed, and the benzene allowed to drop into the nitric acid through a pipette having a very tapering mouth, and only allowing exceedingly small drops to pass through. During this procedure the acid was continually stirred, so as to mix it gradually with the benzene; the water in the calorimeter was also stirred. In this way a known weight of benzene was introduced—1·835 grm. and 3·670 grms. respectively in two different experiments—the operation of pouring in lasting, in all, two minutes.

The cylinder was then corked up and worked through the

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water of the calorimeter, being pushed along by means of the large calorimetric thermometer, which also served to agitate the water at the same time. The progress of this thermometer was followed, also that of the small thermometer immersed in the acid. At the end of six minutes, the two thermometers gave readings agreeing within about one-tenth of a degree, which difference represented the excess of the temperature of the acid over the water in the calorimeter; the variation of temperature in the two experiments being 1·70° and 3·45° respectively. Lastly, the rate of cooling was noted.

The following data were then known. On the one hand, the weights of the water, the platinum, and thermometer reduced to units of water, and also their variation of temperature; on the other hand, the weights of the acid and benzene, and also the thermal variation involved by their combination, which had converted the benzene into nitrobenzene, with the simultaneous production of water.

The heat communicated to the water, platinum, and thermometers may easily be calculated. But an exact calculation of the heat communicated to the mixture of acid and nitrobenzene would require a knowledge of its specific heat. Now, it is sufficient to know that this specific heat approximates pretty closely to ·47, which is the same as that of the acid employed. Thus, in the two experiments in question, the mass of acid and nitrobenzene, reduced to units of water, will be from about 8·5 to 9·5 grms., amounting to about one-sixtieth of the entire heated mass. This fraction is so small as to be of slight importance in the calculation of the heat disengaged. Thus the latter can be estimated within the limits of experimental error without its being necessary to measure more exactly the specific heat of the mixture.

We may thus make a complete calculation of the heat disengaged in the reaction that has taken place in the calorimeter. It is brought by calculation to an equivalent of nitrobenzene, *i.e.* Q, for the weight, $C_6H_5NO_2 = 123$ grms.

The compound formed under these conditions is really nitrobenzene. To make sure of this, it was precipitated, after the experiment, by means of water, and its density taken, which was found to be equal to 1·194 at 14°. Now, Kopp has given the value 1·187 at the same temperature. The difference, therefore, is so slight that the reaction may be accepted as true. This reaction, however, under the conditions of the author's experiment, is complicated by two circumstances, which must be taken into consideration. On the one hand, the nitrobenzene remains dissolved in the excess of acid; and on the other, the reaction itself gives rise to water which must give off a certain amount of heat, owing to its combination with the excess of acid. In order to be able to bring in this last factor,

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a special series of experiments was made for the purpose of measuring the heat disengaged by the same acid, when treated with certain proportions of water, which are increased from a limit below that produced in the experiments given to one a little above it. These experiments were carried out at the same temperature, under the same conditions, and on the same day—each trial being twice repeated. In this way were obtained two pairs of results, from which it was easy to trace the curve representing the heats of hydration of the acid, between limits which comprised the hydration in the preparation of the nitrobenzene. The heat, q, corresponding to the proportion of water formed at the same time as the nitrobenzene may thus be calculated.

2. Lastly, there was selected from amongst these mixtures the one that agreed best with the final data of the experiment relating to the formation of the nitrobenzene. In it was dissolved pure nitrobenzene, in the same relative proportions; the heat of solution was very small. It was brought, by calculation, to the data of the experiment relating to the formation of nitrobenzene, which gave a value, q_1, for the weight, $C_6H_5NO_2$. In short, the number,

$$Q - q - q_1,$$

represents the heat disengaged in the following reaction :—

$$C_6H_6 + (HNO_3 + \cdot 335H_2O) = C^6H_5NO_2 + H_2O + \cdot 335H_2O.$$

The numbers found in the two experiments were, + 35 and + 35·2, average 35·10. In order to make this number apply to true monohydrated acid, HNO_3, we must add to it the heat given off in the reaction of $\cdot 335H_2O$ upon this last acid; or + 1·5, according to the author's experiments.[1]

3. We get then, finally—

C_6H_6 (pure) + HNO_3 (pure) + H_2O disengages + 36·6 Cal.

4. It is easy to deduce from this the *heat of formation of nitrobenzene from its elements*—

$$C_6 \text{ (diamond)} + H_5 + N + O_2 \text{ disengages } + 4{\cdot}2.$$

In short, it was found that—

Benzene, C_6 (diamond) + H_6 = C_6H_6 (liquid)	...	+ 5·0
Nitric acid, H + N + O_3 = HNO_3 (liquid)	...	+ 41·6
Reaction	...	+ 36·6
	Sum	+ 73·2

[1] "Annales de Chimie et de Physique," 5e série, tom. iv. p. 448.

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On the other hand—

$C_6 + H_5 + N + O_2 = C_6H_5NO_2$ (liquid)	x
$H_2 + O = H_2O$ (liquid)	+ 69
Sum ...	+ 69 + x

whence, $x = + 4{\cdot}2$ for 123 grms.

5. *Decomposition by heat.* We know that nitrobenzene is not, properly speaking, an explosive substance. It may be distilled at a certain temperature. If, however, it is subjected to great heat, a powerful reaction is effected between the oxygen of the nitrous molecule and the hydrocarbon elements of the benzene molecule. But the products of this reaction are imperfectly known.

6. The heat of complete combustion of nitrobenzene is calculated from the above data; that of the elements being—

$12C + 12O_2 = 12CO_2$	+ 564·0
$\frac{1}{2}(5H_2 - 5O = 5H_2O)$	+ 172·5
	+ 736·5

On subtracting the heat of formation of nitrobenzene + 4·2 we get—

$\frac{1}{2}(2C_6H_5NO_2$ liquid $+ 25O = 12CO_2 + 5H_2O$ liquid $+ N_2)$ gives off + 732·3 Cal.

This weight relates to 123 grms. For 1 grm. we should get 5952 cal.

2. *Dinitrobenzene*, $C_6H_4(NO_2)_2$.

This substance was prepared by dissolving a known weight of nitrobenzene in nitrosulphuric acid. The apparatus was the same as for nitrobenzene, and the experiment was performed in exactly the same manner. In the platinum cylinder were placed 35 grms. of a mixture previously prepared from 1500 grms. of nitric acid similar to that already described, and 2944 of boiled sulphuric acid.

In these 35 grms. of nitro-sulphuric acid were dissolved: in one experiment, 1·262 grm., and in another 2·534 grms. of nitrobenzene. The elevations of temperature were 73° and 1·44° respectively.

It was proved that the nitrobenzene was entirely converted into dinitrobenzene. The calculations and corrections for obtaining the quantity Q were made as previously (p. 270). The calculation of q (p. 271) is somewhat complicated. In fact, the formation of the dinitrobenzene, in this case, produces two phenomena: it changes the hydration of the nitrosulphuric acid and also alters the relation between the nitric and sulphuric acids, causing the latter to predominate, as a portion of the nitric acid disappears, owing to the fact of the combination. In

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order to estimate correctly the influence of these two effects which would enter into subsequent operations, it was necessary to make several series of experiments. In the first place, it was convenient to measure directly, two experiments being made in each case, the heat disengaged by the mixing of the nitric acid

$$(HNO_3 - \cdot 335\ H_2O)$$

with the boiled sulphuric acid, in four different proportions, chosen so as to comprise within their limits all the cases possible in the experiments which were performed. In this way the curve was obtained for the quantities of heat produced for the whole series of intermediate mixtures.

Then considerable quantities of each of these liquids were prepared and proportions of water added to them, increasing according to distinct ratios, which also comprised within their limits all the cases possible in the experiments. Each time the heat disengaged was measured, and curves constructed for the heats of hydration of these various systems of mixtures.

Thus were obtained the elements necessary for calculating by interpolation the quantity q, in all cases included within the limits of the experiments.

This method is somewhat tedious, but it seemed to be the most suitable for the object in view, viz. the study of a series of analogous formations. If, however, there were only one experiment of this kind to make, it would be preferable to measure the heat given off in three cases only, viz. the mixing of the two acids in their initial proportions; the mixing of the two acids in their final proportions, in which they exist after the performing of the experiments; and lastly, by the addition of water (in the proportion furnished by this experiment) to the mixture of the two acids corresponding to the final proportions.

Lastly, the quantity, q_1 (p. 271), was measured directly, by dissolving a known weight of crystallised dinitrobenzene in a mixture of the two acids and water of proportions similar to those of the final condition of the liquid, that gives rise to the dinitrobenzene. This quantity is negative, as generally happens when solid bodies are dissolved. It was found equal to $-2{\cdot}69$ for $C_6H_4(NO_2)_2$.

We thus arrive definitely at the quantity

$$Q - q - q_1.$$

But this quantity relates to the formation of dinitrobenzene by means of the nitrosulphuric acid of the experiments. In order to apply the reaction to pure nitric acid, we must, in addition, take into account the heat given off by the previous combination of the two acids, and also that by the union of HNO_3 with $\cdot 335\ H_2O$.

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2. It was found, after making all the necessary calculations, that the theoretical reaction—

$C_6H_5NO_2$ (pure) + HNO_3 (pure) = $C_6H_4(NO_2)_2$ (crystal.) + H_2O, disengages + 36·45 and + 36·35 ; average, + 36·4.

This result is to all intents the same as in the formation of mononitrobenzene ; + 36·6 ; or, in other words, *the heat disengaged is proportioned to the number of equivalents of acid linked on to the hydrocarbon.*

The complete formation of dinitrobenzene, starting from benzene—

$$C_6H_6 + 2HNO_3 = C_6H_4(NO_2)_2 + 2H_2O,$$

would give off + 73.

3. These numerical values show that the formation of nitro-compounds involves a considerable loss of energy ; it is much greater than that entailed by the formation of nitric ethers, as we shall presently show.

We can therefore understand why the explosive energy of the latter compounds is greater, and their stability less. We can also understand why nitro-compounds do not act like ethers, the latter being capable of decomposition by potash with re-formation of an alcohol and acid. Potash, which, when combined with dilute nitric acid, gives off only 13·7 Cal., cannot furnish, by a simple reaction, the energy required for the reproduction of the acid and benzene, the union of which, in order to form nitrobenzene, has disengaged 36·5 Cal. This energy, on the contrary, is available in the case of nitric ether and nitroglycerin, which require only 4 to 6 Cal. for the regeneration of each equivalent of acid.

4. Moreover, the figures + 36·5, relating to nitrobenzene, are worthy of notice from another point of view. In fact, this quantity is approximately three-quarters of the heat disengaged in the action of hydrogen on dilute nitric acid, with the formation of nitrous acid, which remains in solution.

H_2 + HNO_3 (dissolved) = H_2O + HNO_2 (dissolved) gives off + 50·5.

In this reaction, the action of the hydrogen is, in certain respects, similar to that of benzene in the formation of nitrobenzene.

5. This shows that the formation of nitrobenzene and similar substances may be compared to oxidation.

On the other hand, the formation of nitric ether and nitroglycerin, which causes the liberation of much less heat, represents a simple substitution of the elements of the acid for the elements of water.

6. The decomposition of nitrobenzene may be effected by sudden heating ; but the products have not been studied.

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7. The formation of dinitrobenzene from its elements—

$$C_6 \text{ (diamond)} + H_4 + N_2 + O_4 = C_6H_2(NO_2)_2 \text{ (dissolved)}$$

gives off 12·7 for 168 grms.

8. The heat of complete combustion of dinitrobenzene (= 168 grms.)—

$$C_6H_4N_2O_4 + O_{10} = 6CO_2 + 2H_2O + N_2,$$

gives off + 689·3 Cal. for 168 grms., which amounts, for 1 grm., to 4103 cal. All these calculations were made for dinitrobenzene obtained without heat; in the action of dinitrobenzene on nitric acid, and without having regard to the mixture of isomeric substances produced in this case. The observations which have been published[1] tend, moreover, to show that various isomeric substances of the same chemical function are formed, causing disengagements of heat almost identical.

3. *Chloronitrobenzene*, $C_6H_4Cl(NO_2)$.

The formation of this compound takes place according to the following equation:—

$$C_6H_5Cl + HNO_3 = C_6H_4Cl(NO_2) + H_2O.$$

It was found that this reaction gives off + 36·4.

We know that several isomeric substances are formed. The heat of solution in a mixture similar to that formed in the reaction was determined.

The details of these experiments may be omitted, as they are similar to those already described.

The heat of chlorination of benzene being unknown, it is not possible to calculate the heat of formation of the above substance from its elements.

4. *Nitrobenzoic Acid*, $C_7H_5(NO_2)O_2$.

The formation of this compound takes place according to the following equation:—

$$C_7H_6O_2 + HNO_3 = C_7H_5(NO_2)O_2 + H_2O.$$

This reaction gives off + 36·4.

We see that this value is nearly constant for the nitration of benzene and all its immediate derivatives. *The formation of nitrobenzoic acid from its elements* is easily calculated if we admit for the heat of formation of benzoic acid the value + 54 (Rechenberg). We then get—

$$C_7 \text{ (diamond)} + H_5 + N + O_4 = C_7H_5(NO_2)O_2 - + H_2 \text{ (liquid)}$$

gives off + 63 Cal. for 167 grms.

The heat of complete combustion of the same substance = 761·5 Cal. for 167 grms., or 3772 cal. for 1 grm.

[1] "Bulletin de la Société Chimique," 2e série, tom. xxviii. p. 530.

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5. *Nitro-derivatives of the Aromatic Series in general.*

1. It has just been shown that the formation of a nitro-compound, belonging to the aromatic series, is generally accompanied by a liberation of heat approximately = +36 Cal.; this number was also obtained by Troost and Hautefeuille for the derivatives of toluene and naphthalene. It will be shown presently that it also holds for the formation of trinitrophenol, otherwise called picric acid.

2. This being admitted, it is easy to give general formulæ for calculating *à priori* the heat of formation of a nitro-compound from its elements, and also its heat of combustion, provided that we possess these data for the original hydrocarbon.

Let A be the heat of formation of the generating substance; + 41·6 Cal. being that of nitric acid; + 36·4 the heat of nitration; and lastly + 69 the heat of formation of water; the equation representing nitration is as follows:—

$$R + HNO_3 = X + H_2O,$$

and from it we arrive at the expression for *the heat of formation of the nitro-compound*, X, or

$$A + 41{\cdot}6 + 36{\cdot}4 - 69 = A + 9 \text{ Cal.}$$

For a binitrated, trinitrated, etc., compound, we shall get—

$$A + 18 \text{ Cal.}; \quad A + 27 \text{ Cal.}; \text{ and generally, } A + 9n.$$

3. In the same way, the heat of complete combustion of a nitro-compound is deduced from that of the original hydrocarbon. The latter being supposed = Q; that of the mononitro-compound, which contains one equivalent less of hydrogen, will be Q − 34·5 − 9 = Q − 43·5; for a dinitro-compound, Q − 87; for a trinitro-compound, Q − 130·5. These formulæ must only be regarded as approximate, as the effect of the nitration is often complicated by the change of physical condition, which should be taken into consideration separately.

4. The large quantity of heat liberated in the formation of nitro-compounds, when using pure nitric acid, enables us to understand the formation of the same compounds when using a mixture of nitric and sulphuric acids. We know for a fact that this mixture is employed, in preference to pure nitric acid, for the preparation of nitro-derivatives; but this is an empirical fact.

The theoretical explanation of it may be given; it results from the difference between the heat of formation of sulphuric derivatives and that of nitro-derivatives, joined to the tendency of sulphuric acid to form a secondary hydrate with the water resulting from the formation of the nitro-compound. For instance, the formation of benzene-sulphonic acid—

$$C_6H_6 + H_2SO_4 = C_6H_6SO_3 + H_2O, \text{ gives off } + 14{\cdot}3 - a;^1$$

[1] a represents the heat of solution of benzene-sulphonic acid in water; a positive quantity amounting to a few Calories.

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whereas that of nitrobenzene—

$$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O, \text{ gives off } + 36{\cdot}6.$$

The difference between these two quantities, $+ 22{\cdot}2 + a$, is enormous and cannot be compensated, either by the difference in the quantities of heat disengaged by the union of H_2O with the excess of nitro-sulphuric acid, in the two experiments, or by the difference in the respective heats of solution, in the same liquid, of nitrobenzene and benzene-sulphonic acid. The difference is further increased by the heat of formation of the secondary sulphuric acid hydrate. Thus the formation of nitrobenzene gives off much more heat than that of benzene-sulphonic acid; the formation of the nitro-derivative, in preference to a sulphuric derivative, is therefore a natural consequence of the general principles of thermo-chemistry.

6. *Trinitrophenol, or Picric Acid and its Salts.*

1. Let us apply these formulæ to picric acid. This acid is derived from phenol, by the replacement of three atoms of hydrogen—

$$C_6H_6O + 3HNO_3 = C_6H_3(NO_2)_3O + 3H_2O.$$

Now the heat of formation of phenol may be estimated either at + 34 Cal., or at + 28 Cal., according to whether we adopt the heat of combustion of Favre and Silbermann (737) or that of M. Rechenberg (743), the difference between which values does not amount to quite one-hundredth.

We will take the mean, 31 Cal., for an equivalent, 229 grms. This being allowed, *the heat of formation of picric acid from its elements*, C_6 (diamond) $+ H_3 + N_3 + O_7$, will be $+ 31 + 27 = +58$ Cal. for 229 grms.; *the heat of combustion* being + 609·5 Cal., according to our formulæ.

2. It is easy to proceed from this to the heat of formation of picrates. Let ammonium picrate be

$$C_6H_2(NO_2)_3ONH_4 = 246 \text{ grms.}$$

According to the calculations,[1] the formation of this body by means of pure acid and ammonia gas—

$$C_6H_3(NO_2)_3O \text{ (solid)} + NH_3 \text{ (gas)},$$

disengages + 22·9 Cal., which gives, for *the heat of formation of the salt from its elements*, for 246 grms.—

$$C_6 + H_6 + 2N_2 + O_7; + 58 + 12{\cdot}2 + 22{\cdot}9 = + 83{\cdot}1 \text{ Cal.}$$

Messrs. Sarrau and Vieille[2] found + 80·1 Cal. for combustion in oxygen, a value agreeing with the former within the limit

[1] Table v. p. 127.

[2] "Comptes rendus des séances de l'Académie des Sciences," tom. xciii. p. 270.

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of experimental errors; as the difference does not amount to half per cent. of the heat of combustion. In fact, *the heat of total combustion of this salt* is, according to calculation + 688 Cal., according to experiment + 691, for 246 grms., or, for 1 grm., 2797 cal.

3. We now come to potassium picrate—

$$C_6H_2(NO_2)_3KO = 267 \text{ grms.}$$

According to table iv., p. 127, the reaction of the acid and base—

$$C_6H_3(NO_2)_3O \text{ (crystal.)} + KHO \text{ (solid)} = C_6H_2K(NO_2)_3O \text{ (solid)} + H_2O \text{ (solid), gives off} + 30{\cdot}5 \text{ Cal.}$$

Admitting that $K + H + O = KHO$ gives off + 104·3, we get for the *heat of formation of potassium picrate from its elements*, for 267 grms.—

$$C_6 + H_2 + K + N_3 + O_7\,;\ + 58 + 104{\cdot}3 + 30{\cdot}5 - 70{\cdot}4 = + 122{\cdot}4 \text{ cal.}$$

Sarrau and Vieille gave, for combustion in oxygen, + 117·5 Cal. The difference in these values amounts to less than one-hundredth of the total heat of combustion, thus being within the limits of error; more so when we take into account that the action of the water, formed in the combustion, on the the potassium bicarbonate has been disregarded by these writers in their calculation, as well as the partial dissociation of the last-named salt.

4. *The heat of total combustion of potassium picrate*, with formation of potassium bicarbonate, amounts to 619·7 Cal., or, for 1 grm., 2321 cal.

5. The *explosive decomposition* of potassium picrate gives rise to complex products: carbonic acid, carbonic oxide, hydrocyanic acid, free hydrogen, nitrogen, marsh gas. The relative proportion of these bodies varies with the conditions.

Thus carbonic acid and marsh gas increase with the pressure, at the expense of the carbonic oxide and hydrogen.

As to the solid residue, it is composed of potassium carbonate and cyanide containing, according to Sarrau and Vieille, the third of the alkaline metal, with a small quantity of carbon. With a density of charge of ·5, the results observed by these writers are represented approximately by the following empiric equation:—

$$16C_6H_2K(NO_2)_3O = 4KCN + 6K_2CO_3 + 21CO_2 + 52CO + 6CH_4 + 22N_2 + 4H_2 + 7C.$$

According to this equation, an equivalent of potassium picrate (267 grms.) would disengage, in decomposing, + 208·4 Cal., or, for 1 grm., 780 cal.

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§ 3. Nitric Ethers from Alcohols properly so called.

General Remarks.

1. Nitric ethers are obtained by the action of nitric acid upon alcohols, accompanied by the substitution of the elements of water for those of acid; 1, 2, 3 to 6, and even more equivalents of acid may take the place of H_2O, $2H_2O$, $3H_2O$ to $6H_2O$, etc., in the alcoholic molecule. For instance—

Nitric ether, $C_2H_4(H_2O) + HNO_3 = C_2H_4(HNO_3) + H_2O$.
Nitroglycerin, $C_3H_2(H_2O)_3 + 3HNO_3 = C_3H_2(HNO_3)_3 + 3H_2O$.

2. The equations representing the formation of nitric ethers are analogous to those for nitro-compounds. But there is a fundamental reaction that characterises the nitric ethers; namely, that they reproduce the acid and original alcohol, under the prolonged influence of water and dilute alkalis, which does not happen in the case of nitro-compounds. Reducing agents also decompose the nitric ethers with reproduction of the original alcohol, whereas, in the case of nitro-compounds, the same agents form compound ammonias.

3. These differences in reactions are correlative with the unequal quantity of heat given off in the action of nitric acid on various organic compounds. If it gives rise to a nitro-derivative (p. 276), it disengages on an average + 36 Cal., or, in the case of an alcohol, properly so called, to an ether, it disengages + 5 to + 6 Cal., and + 11 Cal. at the most, in the case of complex bodies with analogous functions, such as cellulose. It is this that causes the greater instability of nitric ethers. The presence of alkalis, or even moisture, is sufficient to cause a change in them after a little while.

But this circumstance gives greater energy to nitric ethers in their use as explosives; the combustive energy of the nitric acid being much less weakened at the time of its first combination with the organic compound.

This being understood, we will now examine the thermal formation of nitric ethers, beginning with those derived from ordinary alcohol.

1. *Nitric Ether*, $C_2H_4(HNO_3) = 91$ grms.

The formation of this ether was effected in a calorimeter, in a direct manner, by means of pure alcohol and nitric acid, sp. gr. 1·5, and without the addition of any other auxiliary body. The product is approximately the same as would be expected from theory. The experiment, as has been said, can be performed directly, but it is a very delicate operation.

It is effected in the apparatus already described (p. 269), by

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letting pure alcohol fall, in exceedingly minute drops, into nitric acid, which is pure and free from nitrous compounds. With each addition the acid is stirred vigorously, in order to avoid any local elevation of temperature. At the same time the vessel containing the acid is moved about in the water of the calorimeter, so as to cause the gradual absorption of the heat disengaged.

These are essential conditions. When they are very scrupulously observed, we succeed in avoiding all secondary reactions, as well as any disengagement of nitrous vapours, and in converting the alcohol entirely, or almost entirely, into nitric ether, as we can prove by precipitating the mixture, immediately it is formed, by means of water, and collecting and weighing the ether produced.

The addition of urea to the pure nitric acid does not render the experiment more successful; but it is different when a less concentrated acid is used, as in the usual method of preparation of nitric ether.

The only essential condition is that the drops of alcohol should be excessively small, and very rapidly mixed with the mass, so as to avoid any local elevation of temperature, which would promote secondary reactions.

The experiment does not always succeed, and it is better only to take into consideration the calorimetric measurements got by means of a successful reaction. On some occasions 7·5, on others 15 grms. of nitric acid and ·84 grm. of alcohol were experimented upon by the author. After the reaction, the products should immediately be poured into water, otherwise a secondary reaction begins to manifest itself. The latter reaction is also quickly developed when pure nitric ether, prepared beforehand, is dissolved in pure nitric acid, an operation which the author was compelled to perform in the calorimeter, in order to complete the data of the calculations relating to the formation of nitric ether.

2. After all calculations, it is found that the formation of nitric ether—

$$C_2H_6O \text{ (liquid)} + HNO_3 \text{ (liquid)} = C_2H_4(HNO_3) \text{ (liquid)} + H_2O \text{ (liquid)},$$

gives off + 6·2 Cal.; the bodies being supposed pure, separated from each other, and taken at the ordinary temperature.

The heat of solution of nitric ether in water was also measured:

$C_2H_4(HNO_3)$ (1 part) + 180 parts of water gives off + ·99;

whence we get

C_2H_6O (in solution) + HNO_3 (in solution) = $C_2H_4(HNO_3)$ (in solution) + H_2O + water absorbs − 3·2 Cal.

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We see that the thermal effect varies inversely with the dilution, just as in the case of ethyl-sulphuric acid, and those acids allied to it.

The formation of nitric ether is, in this respect, analogous to that of those from organic acids, in which case their production causes absorption of heat, whether the bodies in question be in solution or in a pure state.[1]

But, on the contrary, the formation of nitric ether from concentrated acid gives rise to disengagement of heat. This opposition results from the great difference of energy existing between nitric acid in the pure state and that diluted with water.

3. The formation of nitric ether from its elements—

$$C_2 \text{ (diamond)} + H_5 + N + O_3 = C_2H_4(HNO_3) \text{ (liquid)},$$

gives off + 49·3 Cal. for 91 grms., or, for 1 grm., 542 cal.

4. *Decomposition.*—Nitric ether may be distilled with great regularity, but care must be taken to avoid all local overheating. The approach of a flame, or even a temperature of about 300°, causes the ether to explode with violence. A terrible accident, which happened at a chemical works at St. Denis, has shown the dangers attendant upon the handling of large quantities of this ether. The products of this explosion have not been analysed. The oxygen contained in the compound is, moreover, insufficient to oxidise the carbon and hydrogen, even supposing the first body to be converted only into carbon monoxide. Admitting the following reaction—

$$C_2H_4(HNO_3) = 2CO + H_2O + 3H + N,$$

the composition of the liquid ether, with the formation of liquid water, would give off + 71·3 Cal. for 91 grms. If the ether and water were in the gaseous form, the figures would be slightly different, amounting, for 1 grm., to 787 cal.

5. The *heat of total combustion* of nitric ether by means of pure oxygen—

$$\tfrac{1}{2}[2C_2H_4(HNO_3) + 7O = 4CO_2 - 5H_2O - N_2],$$

gives off + 311·2 Cal. for 91 grms., or 3420 cal. for 1 grm.

2. *Nitroglycerin*, $C_3H_2(HNO_3)_3$ = 227 grms.

1. Nitroglycerin was prepared in a calorimeter, by means of nitrosulphuric acid, and under conditions similar to those recently described by M. Champion; conditions under which the product amounts to only four-fifths of the theoretical value, owing to unavailable secondary oxidations. Quantities of 1·201 grm. and 1·934 grm. of glycerin were experimented upon. It

[1] "Annales de Chimie et de Physique," 5e série, tom. ix. p. 344.

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was contained in a little capsule, accurately weighed, and poured drop by drop into the middle of the nitrosulphuric mixture. When a sufficient quantity of glycerin had been poured out the capsule was re-weighed; the loss in weight showed the quantity of glycerin introduced.

2. All necessary calculations having been made, it was found that the ordinary reaction, *i.e.* the case in which the substances are taken in their actual condition—

$$C_3H_8O_3 + 3HNO_3 = C_3H_2(HNO_3)_3 + 3H_2O,$$

gives off + 14·7; or + 4·9 for each equivalent of acid that has entered into combination.

These figures, which are rather below those obtained for nitric ether, show that both the acid and the glycerin have preserved almost all their reciprocal energy throughout the reaction, a circumstance which explains the remarkably easy decomposition of nitroglycerin and the formidable effects thereof.

3. Again, we find that

$C_3H_8O_3$ (in solution) + $3HNO_3$ (diluted) = $C_3H_2(HNO_3)_3$ (pure) + $3H_2O$ (liquid), absorbs − 8·8, or − 2·9 × 3.

Therefore we have thermal inversion, arising from the solution of the substances; exactly as in the case of nitric ether. This is another point of resemblance between nitroglycerin and ethers formed from organic oxy-acids.

4. *The heat of formation of nitroglycerin from its elements* may be calculated from its heat of formation, as deduced from the heat of combustion which was observed by M. Louguinine. We thus find

C_6 (diamond) + H_5 + N_3 + O_9 gives off + 98 Cal. for 227 grms., or 432 cal. for 1 grm.

5. The *heat of total combustion* and the *heat of complete decomposition* are, in this case, interchangeable terms, since nitroglycerin contains an excess of oxygen—

$$\tfrac{1}{2}[2C_3H_2(HNO_3)_3 = 6CO_2 + 5H_2O + 3N_2 + O].$$

Sarrau and Vieille have verified the reality of this reaction.

From the preceding data, we find that the heat of combustion is equal to + 356·5 Cals., or, for 1 grm., 1570 cal.

Sarrau and Vieille obtained + 360·5 Cal.; a value agreeing as nearly as could be expected.

Nitroglycerin is decomposed differently if it is ignited as dynamite, *i.e.* an intimate mixture of silica and nitroglycerin, and if the gases which are formed are allowed to escape freely, under a pressure nearly equal to that of the atmosphere. Sarrau

[1] "Comptes rendus des séances de l'Académie des Sciences," tom. xciii. p. 270.

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and Vieille obtained under these conditions, for 100 volumes of gas—

NO	...	...	...	48·2
CO	...	...	...	35·9
CO_2	...	...	...	12·7
H	...	...	...	1·6
N	...	...	...	1·3
CH_4	...	...	...	0·3

These conditions are similar to those under which a mining charge, simply ignited by the cap, burns away slowly under a low pressure; this is called a miss-fire.

3. *Nitromannite*, $C_6H_2(HNO_3)_6 = 452$ grms.

1. This substance was prepared by means of nitrosulphuric acid. The reaction is slow and somewhat prolonged. One grm. of mannite and 30 grms. of acid liquid were operated upon. Assuming the reaction to have been complete, the numbers that were observed gave + 23·5 Cal. for the reaction

$$C_6H_{14}O_6 + 6HNO_3 = C_6H_2(HNO_3)_6 + 6H_2O,$$

or + 3·92 Cal. per equivalent of fixed nitric acid.

2. *The heat of formation of nitromannite from its elements* is calculated from the above figures, together with the heat of formation of mannite, as deduced from its heat of combustion (760 Cal.), which was obtained by M. Rechenberg. We thus find—

C_6 (diamond) + H_8 + N_6 + O_{18} gives off + 156·5 Cal. for 452 grms.

Sarrau and Vieille deduced from the heat of combustion of nitromannite itself its heat of formation, + 165·1 Cal. for 452 grms., a value sufficiently close to the above if we take into account the heats of combustion given below; for the difference between the heats of combustion calculated and those found by experiment does not amount to one-hundredth.

The heat of combustion of nitromannite is the same as its *heat of decomposition*, this substance containing, like nitroglycerin, an excess of oxygen—

$$C_6H_2(HNO_3)_6 = 6CO_2 + 4H_2O + {}^3N_2 + O_2.$$

This reaction gives off, according to calculation, 564 + 276 − 156·1 = + 683·9 Cal. for 452 grms.

Sarrau and Vieille found directly 678·5 Cal., or, for 1 grm., 1501 cal.

4. *Heat of Formation of Nitric Ethers in general.*

1. It is desirable to treat here of ethers formed from true alcohols, which have simple functions (p. 268).

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According to the preceding data, the formation of a nitric ether, by means of alcohol and nitric acid, would give off, on an average, + 5 Cal. for each equivalent of fixed nitric acid. This quantity may be used to calculate the heat of formation and the heat of combustion of nitric ethers that have not as yet been studied.

2. Let us suppose an ether to be formed from an alcohol, represented by the letter R; the ether being—

$$R + nHNO_3 - nH_2O.$$

The heat of formation of the ether from its elements will be deduced from the heat of formation, A, of the alcohol by the following formula:—

$$A + 41{\cdot}6n + 5n - 69n = A - 22{\cdot}4n.$$

It is lower than the heat of formation of the original body; a fact which distinguishes ethers from nitro-compounds (p. 276), the heat of formation of which, on the contrary, exceeds that of the original substance by + 9*n* Cal. The difference, which is 31·4 Cal. for each equivalent of fixed nitric acid, denotes the excess of energy of a nitric ether over that of an isomeric nitro-derivative, formed from the same original substance; benzyl nitrate, for instance, as compared with nitrobenzyl alcohol.

3. *The heat of decomposition* of a nitric ether can thus be calculated *à priori*, if its products be known; as in the case in which the substance contains an excess of oxygen.

4. *The heat of total combustion* of a nitric ether is deduced in all cases from that of the original alcohol. This being equal to Q, the formula of the ether deduced from *n* equivalents of nitric acid will contain *n*H less, and its heat of combustion will be—

$$Q - 34{\cdot}5n + 22{\cdot}4n = Q - 12{\cdot}1n.$$

If, for example, we take nitroglycerin ($n = 3$), we shall get Q = 392·5 Cal., according to M. Louguinine's data for glycerin. The heat of total combustion of nitroglycerin, calculated by the formula, will then be + 356·2. Messrs. Sarrau and Vieille found by experiment, + 360·5. The discrepancy amounts to one-hundredth, and includes both the error made in the heat of combustion of glycerin and also that of nitroglycerin.

5. In order to make these points clear, let us calculate, according to the above formula, the formation of methyl nitrate—

$$C + H_3 + N + O_3 = CH_2(HNO_3).$$

The formation of methyl alcohol from its elements, A, = 62; we shall therefore get + 39·6 for *the formation of methyl nitrate from the elements.*

The heat of total combustion of this ether will be—

+ 157·9 for 77 grms., or 2050 cal. for 1 grm.

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Assuming the following equation to represent the *explosive decomposition* of this ether—

$$\tfrac{1}{2}[2CH_2(HNO_3) = CO_2 + CO + N_2 + 3H_2O],$$

the heat disengaged would be + 123·8 Cal. for 77 grms. But if we prefer to assume that the decomposition answers to the formula—

$$\tfrac{1}{2}(2CO_2 + N_2 + H_2 + 2H_2O),$$

we shall get + 124·1 Cal., which is, to all intents, the same.

This gives for 1 grm., 1602 cal.

6. Let us also take the formation of ethylene nitrate—

$$C_2H_2(HNO_3)_2,$$

A, = 111·7, derived from the heat of combustion of glycol, as observed by M. Louguinine. The quantity + 66·9 Cal. for 1 equivalent = 152 grms. thus expresses the *heat of formation from the elements.*

The *heat of decomposition* will in this case be identical with the *heat of total combustion*—

$$C_2H_2(HNO_3)_2 = 2CO_2 + 2H_2O + N_2$$

gives off + 258·8 Cal. for 152 grms., or, for 1 grm., 1956 cal.

Since it does not contain any excess of oxygen, ethylene nitrate must therefore be an explosive substance with maximum effect.

5. *Nitric Derivatives from Complex Alcohols.*

1. We may now proceed to nitric derivatives produced from alcohols of complex function. The only ones that have been studied from a thermal point of view are cellulose and its isomers, which are alcoholic ethers, themselves derived from glucose, an aldehydic alcohol.[1]

2. These compounds, when treated with water or alkalis, do not decompose in a simple manner, *i.e.* so as to reproduce the original nitric acid and cellulose; but give rise to complex reactions, which are imperfectly known, and in which the aldehydic function seems to play a part.

On the other hand, when treated with reducing agents, so as to cause the destruction of the nitric acid, they reproduce the cellulose, which still retains its original properties.

3. The greater stability possessed by this class of nitric derivatives, when treated with agents of hydration, corresponds, as we shall show, to the greater heat of nitration, *i.e.* to the more considerable loss of energy in the act of preparation.[2]

Only two derivatives of this order have been studied from a thermal point of view, viz. gun-cotton and xyloidin.

[1] See the author's "Traité élémentaire de Chimie organique," tom. i. p. 371. 1881. Dunod.

[2] See the theorem on p. 123.

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6. *Nitrostarch* (*Xyloidin*).

1. This body answers to the formula in the following equation:—

$$C_6H_{10}O_5 + HNO_3 = C_6H_8O_4(HNO_3) + H_2O,$$

or rather, to a multiple of this formula, if we admit that starch is itself a condensed body, derived from several molecules of glucose—

$$nC_6H_{12}O_6 - nH_2O = C_6nH_{10}nO_5n.$$

Since the value of n is not definitely known as yet, it is convenient, for the sake of simplicity, to reduce the data to a value of $n = 1$.

2. Nitrostarch was prepared from a mixture of dry starch and nitric acid, sp. gr. 1·5. It was found that the reaction—

$$C_6H_{10}O_5 + HNO_3 = C_6H_8O_4(HNO_3) + H_2O,$$

gives off 12·4 Cal, the nitrostarch separating out in a solid form.

This is almost the same value for each equivalent of fixed acid as we get for gun-cotton.

It will be noticed that this value is double that got for nitric ether and nitroglycerin, while it is only a third of the heat disengaged in the formation of nitrobenzene. Gun-cotton and xyloidin behave as substances intermediate between nitro-compounds and normal nitric ethers; they also resist alkalis far better than nitric ethers.

3. The *heat of formation of nitrostarch from its elements* may be calculated, if we admit, with M. Rechenberg, that the heat of total combustion of starch is equal to + 726 Cal.; its heat of formation will be equal then to 183 Cal. We shall find, then, that

$$C_6 + H_9 + N + O_7 \text{ gives off } + 183 + 41{\cdot}6 + 12{\cdot}4 - 69 = + 168 \text{ Cal. for 207 grms.},$$

or, for 1 grm., 812 cal.

4. The *heat of decomposition* could only be calculated if the products of this decomposition were given; but they have not as yet been studied, and the quantity of oxygen contained in the compound is far from being sufficient for its complete combustion.

5. The *heat of total combustion* is equal to 706·5 Cal. for 207 grms., or, for 1 grm., 3413 cal.

7. *Pernitro-cellulose, or Gun-cotton.*

1. This substance results from the action of nitric acid upon cellulose, the latter being taken under the particular form of cotton. Nitric acid replaces the elements of water of the cellulose, without altering in any way its physical appearance.

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Several compounds may in this way be formed, distinguished from each other by the amount of nitric acid which they contain. For the sake of simplicity they are generally classified under three heads—

Mononitrocellulose	$C_6H_9O_4(HNO_3)$
Dinitrocellulose	$C_6H_8O_3(HNO_3)_2$
Trinitrocellulose	$C_6H_4O_2(HNO_3)_3$

but these proportions are not always strictly observed. As a matter of fact, the formula for cotton is higher than $C_6H_{10}O_5$; it is a multiple of this quantity. Moreover, the quantity of nitric acid indicated by the third formula is somewhat higher than the maximum quantity that is ever united to the cotton; in fact, the latter falls appreciably below this value, according to most exact analyses and syntheses. As no other thermal experiments have as yet been made with gun-cotton, we propose to discuss this compound in detail.

Admitting the formula of cellulose to be $C_{24}H_{40}O_{20}$, the formulæ of gun-cotton that best represent that formed in the experiments are the following:—

$$C_{24}H_{20}O_{10}(HNO_3)_{10}, \text{ or } C_{24}H_{18}O_9(HNO_3)_{11}.$$

The slight difference between the two formulæ is owing to the small quantity of carbon retained in the ashes under the form of carbonate, which is disregarded in the second formula. The latter, however, seems, on the whole, preferable.

2. Gun-cotton was prepared in a calorimeter by means of nitrosulphuric acid, and under the same conditions as those in the preparation of nitrobenzene (p. 270). 1·188 and 1·241 grm. of dry cotton were used. The reaction being prolonged, the experiment was each time stopped at the end of twenty minutes. The gun-cotton was then washed, dried, and weighed, which gave the proportion of acid fixed. This proportion was found to be somewhat below that corresponding to complete nitration, but the experiment had not lasted long enough for this. In each case 9 equivalents of nitric acid, instead of 10 or 11, were fixed on to $C_{24}H_{40}O_{20}$.

From the results obtained, we calculate the heat given off to be 102 Cal. for $9HNO_3$; or, + 11·4 Cal. for each equivalent of fixed nitric acid. We may, therefore, admit that the fixing of $11HNO_3$, according to the formula

$$C_{24}H_{40}O_{20} + 11HNO_3 - 11H_2O,$$

would disengage + 125·4 Cal.; or + 114 Cal. for the formula

$$C_{24}H_{40}O_{20} + 10HNO_3 - 10H_2O,$$

which represents the conventional composition of gun-cotton.

3. The value + 11·4 is very near that of + 12·4 found for nitrostarch, which justifies us to a certain extent in assuming

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that for each nitric equivalent fixed on to a carbohydrate, a heat of about + 12 Cal., on an average, is liberated. This value, it may be repeated, is double that of the heat of formation of the nitric ethers properly so called.

4. In order to deduce from this the heat of formation of gun-cotton from its elements, it would be necessary to determine the heat of formation of cotton itself, which is at present unknown.

5. Messrs. Sarrau and Vieille have measured the *heat given off in the decomposition of gun-cotton*. As this varies with the conditions, they give results for the decomposition that furnishes the following products, $15CO + 9CO_2 + 11H + 11N + 9H_2O$. From this we deduce, for the heat of total combustion of gun-cotton—

$C_{24} + H_{43} + 11N + O_{43}$ (= 1143 grms.), the value + 633 Cal.

On oxidising the gun-cotton by means of ammonium nitrate, they obtained a result leading to + 698 Cal. The discrepance in the two values shows the difficulty of carrying out experiments which are of this nature, and are based upon complicated reactions. The above figures may, however, serve as approximate data until the discovery of a more definite method.

According to the first value, the *heat of total combustion of gun-cotton* in free oxygen would be 562·5 cal. for 1 grm.

The heat of formation from its elements would be 624 Cal. for 1143 grms.

6. We will now say a few words about the explosive decomposition of gun-cotton conducted in a closed vessel and at constant volume; this formed the subject of a carefully studied and very interesting paper by Messrs. Sarrau and Vieille.[1] They found that the volume of the gases (reduced to 0° and 760 mms.), and also their relative proportion, vary with the density of charge, *i.e.* with the pressure developed at the moment of the explosion. These are some of the results—

Density of charge		0·01	0·023	0·2	0·3
Volume of gases (reduced) per grm. of material		658·5	670·8	682·4	—
Composition of the gases per 100 volumes	CO	49·3	43·3	37·6	34·7
	CO_2	21·7	24·6	27·7	30·6
	H	12·7	17·2	18·4	17·4
	N	16·3	15·9	15·7	15·6
	CH_4	0·0	trace	0·6	1·6

From this table it follows that the quantities of carbonic acid and hydrogen increase with the density of charge; whereas that of carbon monnade diminishes. We notice, moreover, the production of an appreciable and increasing quantity of marsh gas.

[1] "Comptes rendus des séances de l'Académie des Sciences," tom. xc. p. 1058.

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If we disregard it, the following formulæ express these facts:—

$$\text{i. } C_{24}H_{13}O_9(HNO_3)_{11} =$$

Density 0·01	...	$33CO + 15CO_2 + 8H_2 + 21H_2O + 11N_2$
„ 0·023	...	$30CO + 18CO_2 + 11H_2 + 18H_2O + 11N_2$
„ 0·21	...	$27CO + 21CO_2 + 14H_2 + 15H_2O + 11N_2$
„ 0·2	...	$26CO + 22CO_2 + 15H_2 + 14H_2O + 11N_2$

Thus, with low densities of charge, the reaction produces volumes of carbonic oxide, carbonic acid, and hydrogen, which are represented, to all intents, by the simple ratio, 4, 2, 1, whereas, under greater densities, the quantities produced approximate more and more clearly to the limit—

$$24CO + 24CO_2 + 17H_2 + 12H_2O + 11N_2.$$

We may assume that the last formula fairly represents the mode of decomposition realised under ordinary conditions of practice in which gun-cotton, with great densities of charge, is used.

It will be observed that neither nitric oxide nor any other nitrous vapours are produced in the explosive decomposition of gun-cotton in a closed vessel.

7. It is otherwise when the gun-cotton is ignited by means of a red-hot wire, and the gases are allowed to escape freely, under a pressure very nearly equal to that of the atmosphere, so as to prevent their being heated. Under these conditions, which are those of a miss-fire, the above-mentioned writers obtained per 100 vols.

See table, p. 33.

NO	...	...	...	24·7
CO	...	...	...	41·9
CO_2	...	...	...	18·4
H	...	...	...	7·9
N	...	...	...	5·8
CH_4	...	...	...	1·3

This again shows the multiplicity of decomposition that the same explosive substance can undergo (see p. 7).

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CHAPTER IX.

DIAZO-COMPOUNDS—DIAZOBENZENE NITRATE.

§ 1. General Remarks.

1. Nitrogenous organic compounds are derived from mineral substances containing nitrogen by their combustion with non-nitrogenous substances, this combustion being accompanied by the separation of the elements of water.[1]

We thus obtain—either derivatives from the hydrogenated compounds of nitrogen, such as those from ammonia, alkalis, and amides, which were discussed in Chapter VI., and those from hydroxylamine, with which we have nothing to do at this point, or derivatives from oxygenated compounds of nitrogen, such as the nitric derivatives, *i.e.* the nitric ethers and nitro-compounds discussed in Chapter VIII.; to these we may add, on the same principle, nitrous derivatives, nitrous ethers, nitroso-compounds, not as yet used as explosive substances, and hyponitrous derivatives, hardly known.

2. The hydrogenated and oxygenated compounds of nitrogen may also be associated two and two, three and three, etc., in the formation of the same organic derivative; they form bodies of complex function, which are designated by the names diazo-, triazo-, etc., derivatives.

Now, compounds of this order seem to be called upon to play some part in the application of explosive substances. Let us take the simplest of them, viz. those derived from ammonia and nitrous acid, associated simultaneously with the same organic compound. Such a one is diazobenzene, derived from phenol and the two above-mentioned nitrogenous compounds—

$$C_6H_6O + HNO_2 + NH_3 - 3H_2O = C_6H_4N_2.$$

Such a body contains the nitrogenous residues both of ammonia

[1] "Traité élémentaire de Chimie Organique," by MM. Berthelot and Jungfleisch, tom. ii. p. 313. 1881. Dunod.

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and of nitrous acid. Under certain conditions it takes up the elements of water, reproducing phenol and free nitrogen—

$$C_6H_4N_2 + H_2O = C_6H_6O + N_2.$$

In this case the nitrogen is produced by the reciprocal reaction of the two nitrogenous components, precisely as in its production from the direct reaction of ammonia and nitrous acid, the original generators.

3. The heat disengaged in the formation of a diazo-compound is far below that which would be produced in the formation of nitrogen by the direct reaction of ammonia and nitrous acid. In other words, the water eliminated in the original reaction that engenders the diazo-compound, did not at the time of its formation give off the same quantity of heat as if it had been formed directly by the reaction of the two nitrogenous generators in a free state. Thus, the diazo-compound contains an excess of energy which renders it liable to sudden decomposition. It is a highly explosive body. This theory leads us to foresee the explosive properties of diazo-compounds. Only one of these has, as yet, been studied from this point of view; namely, diazobenzene; and its properties fully bear out the forecasts of this theory. For purposes of application diazobenzene nitrate is especially worthy of study. It is a crystalline compound, more easily handled than diazobenzene itself, and containing, besides, a greater amount of energy, on account of the additional presence of the nitric acid, which is calculated to exercise an oxidising action upon the carbon. M. Vieille and the author have studied its thermal and mechanical properties.

§ 2. Diazobenzene Nitrate.

1. Diazobenzene nitrate is an explosive substance which is solid and crystalline. It answers to the formula—

$$C_6H_5N_2NO_3,$$

its equivalent being equal to 167.

It has been proposed to use this body as a priming. In virtue of its various modes of decomposition it is now employed in industry in the manufacture of colouring matters.

M. Vieille and the author have studied its preparation, stability, density, and also its detonation (both with respect to the heat disengaged and also to the nature of the products), its heat of combustion and of formation from the elements, and lastly, the pressures developed by its detonation in a closed vessel; but the examination of this last branch of the subject will be reserved for Book III.

2. Preparation. Aniline is the starting-point in the pre-

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paration of diazobenzene; that used in the experiments was of excellent quality as regards purity.

3. Diazobenzene nitrate was prepared by the well-known (Griess's) process of treating aniline nitrate with nitrous acid. Five to 6 grms. of pure aniline nitrate were taken. This was pounded and mixed with a little water, so as to form a paste, which was placed in a tube surrounded with a refrigerating mixture. A current of nitrous acid was then slowly introduced into it, the mixture being continually stirred, so as to carefully avoid any heating. The liquid at first turns a deep red, but afterwards assumes a lighter tint. As soon as it begins to give off nitrogen the operation is stopped. We then add to the liquid its own volume of alcohol, and subsequently an excess of ether, which precipitates diazobenzene nitrate. The latter is washed upon a cloth with pure ether; it is then pressed and dried in vacuo. In this way 67 per cent. of the theoretical yield was obtained.

4. *Stability.* Diazobenzene nitrate placed in a dry atmosphere, and protected from the light, has been preserved for two months and longer, without alteration, When exposed to daylight, it becomes pink, and then changes more and more, although slowly.

This alteration is much more marked under the influence of moisture; the compound first emits an odour of phenol, and assumes a peculiar tint; then, after a time, it expands, becoming black and giving off gases. Merely breathing upon this compound will cause it to turn red.

On contact with water, it is immediately destroyed, giving off nitrogen, phenol, and various other products—

$$C_6H_5N_2NO_3 + H_2O = C_6H_6O + N_2 + HNO_3.$$

Diazobenzene nitrate is quite as sensitive to a shock as mercuric fulminate; when struck by a hammer, or rubbed rather vigorously, it detonates. It is much more susceptible to the influence of moisture and light than the fulminate.

5. When heated beyond 90°, diazobenzene nitrate detonates with extreme violence. Below this temperature it decomposes gradually and without detonation; at least, when it is heated in small quantities. We see by this that diazobenzene nitrate is much more sensitive to heat than mercuric fulminate—a compound whose point of deflagration under the same conditions is about 195°.

6. *Density.* The density of diazobenzene nitrate has been found to be equal to 1·37, by means of the volumenometer, or one-third that of the fulminate. A high pressure slowly brought to bear on this body brings it to an apparent density approximating to unity.

7. *Composition.* 0·5 grm. burnt by detonation in an atmosphere of pure oxygen, gave the theoretical proportion of

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carbonic acid to within about $\frac{1}{300}$th (less). There was neither carbon monoxide nor any other combustible gas in the residue.

Experiments were made with 0·5 grm., suspended by means of a metallic wire, capable of being made red-hot by an electric current, in the centre of a platinum vessel filled with pure oxygen. The average of two experiments gave 0·4296 carbonic acid; the quantity calculated being 0·43 grm.

8. *Heat of formation from the elements.* According to the total heat of combustion, which will be given further on—

$$C_6 \text{ (diamond)} + H_5 + N_3 + O_3 = C_6H_5N_2NO_3, \text{ absorbs} - 47{\cdot}7 \text{ Cal.}$$

The formation of nitric acid, $H + N + 3O = HNO_3$ (liquid), gives off + 41·6 Cal.; we therefore conclude that, taking into account the nitric acid previously existing—

$$C_6 + H_4 + N_2 + HNO_3 \text{ (liquid)} = C_6H_5N_2NO_3 \text{ absorbs} - 89 \text{ Cal.}$$

This value gives a more exact notion of the heat of formation of diazobenzene itself. But we have to subtract from it the heat disengaged by the combination of the diazobenzene with the nitric acid. But free diazobenzene is itself a liquid body, too imperfectly defined to have enabled one to study it.

However this may be, these negative values correspond very well with the explosive properties so characteristic of this compound.

The decomposition of diazobenzene nitrate by means of water, with the reproduction of dissolved phenol and dilute nitric acid—

$$C_6H_5N_2NO_3 + H_2O = C_6H_6O + N_2 + HNO_3 \text{ (diluted)},$$

gives off + 108·1 Cal.

9. *Heat of detonation.* This term is used to express the heat given off by the simple explosion of diazobenzene nitrate, an explosion that gives rise to complex products.

This explosion was effected in an atmosphere of nitrogen, in a steel bomb lined with platinum; it was ignited by means of the galvanic heating of a fine platinum wire. The nitrate was placed in a little tin cartridge, which was suspended in the centre of the bomb, so as to avoid local actions arising out of contact with the walls.

The results (in two experiments which were made upon 1·6 grms.) were: 688·9 and 686·6 Cal.; the mean being 687·7 Cal. per kgm., or 687·7 cal. per grm. This gives for an equivalent (= 167 grms.) + 114·8 Cal., at a constant volume.

10. The volumes (reduced) of the gases produced were 815·7 and 820 litres; average = 817·8 litres per kgm., or 136·6 litres per equivalent (167 grms.).

11. Under the conditions of the experiments that were made,

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i.e. with a low density of charge, the composition of these gases was as follows:—

HCN	...	3·2	or, for 136·6 litres	...	4·4
CO	...	48·65	„	...	66·4
CH_4	...	2·15	„	...	2·9
H	...	27·7	„	...	37·9
N	...	18·3	„	...	25·0
		100·0			136·6

It may be observed in this explosive decomposition—

(*a*) That a considerable quantity of hydrocyanic acid is formed.

(*b*) That the whole of the oxygen, to within about one-hundredth, is found as carbon monoxide; *i.e.* the carbon takes up all the oxygen, while water is not formed to any appreciable extent in the detonation.

(*c*) That *only* three quarters of the nitrogen is disengaged in a free state, one-fifteenth being given off as hydrocyanic acid. The remainder is contained in the carbonaceous products of the explosion; a fraction, however—about one-fifth of the surplus nitrogen—is found condensed as ammonia, as will be shown presently; but, all allowance being made, the greater part (about half an equivalent) remains united with the carbon, under the form of a special fixed nitrogenous compound.

(*d*) That the free hydrogen amounts to almost three and a half equivalents out of the five equivalents that the substance contained; one half equivalent goes to form marsh gas, another half equivalent goes to form ammonia and hydrocyanic acid, and the last half equivalent remains united with the carbon.

(*e*) That exactly half the carbon forms carbon monoxide. A ninth of the remainder goes to form hydrocyanic acid and marsh gas.

(*f*) That the solid residue contains nearly half ($\frac{4}{9}$) its weight of carbon. A ninth of the remainder enters into the acid and marsh gas. The gross composition of the residue approximates pretty closely to the proportions represented by $C_5H_2N_2$; it is therefore a carbon rich in nitrogen and hydrogen, combined under the form of condensed and polymerised bodies of the paracyanogen type.

(*g*) That the gaseous products comprise, according to the calculation of the preceding analyses, 75·9 per cent., by weight, of the substance. A direct experiment effected by observing the loss of weight of the apparatus when the gases are allowed to escape freely after the explosion, gave 75·6.

(*h*) That, therefore, the solid residue comprises 24·1 per cent. by weight. It exists as charcoal reduced to an impalpable powder which is very voluminous and emits an ammoniacal odour. The quantitative analysis of free ammonia in the

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residue was effected without heat by means of the Schloesing process, when it was found to represent ·011 grm. per gramme of the explosive compound. In the gases themselves, we found 0·00042 grm. of ammonia.

12. The following table sums up these results, the weights being expressed in parts per thousand:—

Nitrogen ...	free	189·7			
	in the form of HCN ...	16·7	215·5		
	„ „ NH_3 ...	9·2			251·2
	combined in the charcoal ...		35·6		
Oxygen ...	in the form of CO ...	...	...		287·6
Hydrogen	free	20·5			
	in the form of CH_4 ...	3·2	26·9		
	„ „ HCN ...	1·2			29·9
	„ „ NH_3 ...	2·0			
	combined in the charcoal ...	...	3·0		
Carbon ...	in the form of CO ...	215·8			
	„ „ HCN ...	14·3	239·6		
	„ „ CH_4 ...	9·5			431·3
	„ „ fixed matter	...	230·3		
Gaseous products	... 769·7	1000			
Residue	... 230·3				

The result, 769·7, is higher than the weight of gas given above (758·6), as it includes the ammonia.

13. *Equation of decomposition.* We see, from this table and from the discussion that arose when these gases were being studied, that, if we disregard the complications caused by secondary formations (hydrocyanic acid, ammonia, marsh gas), the principal reaction is reduced to the following:—

$$C_6H_5N_2NO_3 = 3CO + 3C + 5H + 3N.$$

In reality, about one-tenth of the carbon that is not combined with the oxygen, remains united with the hydrogen and nitrogen, in a gaseous form, constituting marsh gas and hydrocyanic acid. One-third of the hydrogen goes to form these same gases, together with ammonia and fixed compounds. Lastly, one-fourth of the nitrogen goes to form ammonia, hydrocyanic acid, and nitrogenised charcoal.

14. The simple decomposition of diazobenzene nitrate so as to give carbon monoxide and free elements—

$$3CO + 3C \text{ (diamond)} + 5H + 3N,$$

should disengage 201·6 Cal. at constant pressure; *i.e.* 204·7 Cal. at constant volume according to the heat of total combustion, instead of + 114·8, which was actually found. This proves that the formation of secondary products has absorbed − 89·9 Cal.

Such an absorption of heat results principally from the formation of the nitrogenised charcoal; the exothermal formation of ammonia and marsh gas almost counterbalancing the endothermal formation of hydrocyanic acid.

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This fact is in accordance with the general result; according to which the carburets, that are only slightly hydrogenated, and the carbonaceous substances, retain a considerable portion of the energy of their complex generators; their energy exceeds more or less that of the elements themselves.

This remark, which was at first made concerning acetylene, has a very wide application in pyrogeneous decompositions; it explains the singular conditions under which certain endothermal compounds are generated, at the very moment that organic compounds are destroyed by heat.

15. *Heat of total combustion.* Combustion was started by galvanic ignition of a fine platinum wire, in an atmosphere of pure oxygen. It gave off, for 167 grms. (1 equiv.), + 783·9 Cal. at constant volume (two experiments), which gives 782·9 Cal. at constant pressure; or, for 1 grm., 469·4 cal. at constant volume.

If the oxidation is complete, the reaction may be represented by the following equation:—

$$\tfrac{1}{2}[2C_6H_5N_2NO_3 + 23O = 12CO_2 + 5H_2O + 3N_2]$$

The heat of combustion by oxygen with reproduction of nitric acid—

$$C_6H_5N_2NO_3 + 7O_2 = 6CO_2 + 2H_2O + N_2 + HNO_3,$$

would give off, in addition, the heat of formation of nitric acid combined with two equivalents of water—

$$HNO_3, 2H_2O,$$

or + 46·6; altogether + 829·5 Cal.

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CHAPTER X.

HEAT OF FORMATION OF MERCURIC FULMINATE.

1. We know the part played by mercuric fulminate in the manufacture of *priming*. This compound probably belongs to the class of diazo-compounds. M. Vieille and the author have studied its heat of decomposition, from which may be determined the heat of formation.

2. The fulminate used in our experiments was taken from the regulation detonators used by the Government. These detonators contain 1·5 grm. of fulminate, and are manufactured at Arras.

3. Its analysis gave—

					Calculated.
C	...	8·35	C	...	8·45
O	...	11·05	O	...	11·30
N	...	9·60	N	...	9·85
Hg	...	71·30	Hg	...	70·40
		100·34			100·0

The mercury was weighed as sulphide, the substance having previously been oxidised by means of hydrochloric acid and potassium chlorate. It is slightly in excess. This fact arises from the presence of a small quantity of metallic mercury mechanically mixed with the substance.

The nitrogen and hydrogen were determined volumetrically after detonation of the substance. The hydrogen may be disregarded, its presence being due to some accidental circumstance.

The carbon and oxygen were determined together, as carbon monoxide after detonation, by which only slight traces of carbonic acid are produced. In fact, five experiments gave for one gramme of the substance, 234·2 cc., containing, per 100 volumes—

CO_2	...	...	...	...	...	0·15
CO	...	...	...	...	...	65·70
N	...	...	...	...	...	32·26
H	...	...	...	...	...	1·80

Theory requires 235·6 cc.

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The detonation should be effected in an atmosphere of nitrogen in order to avoid the partial oxidation of the carbon monoxide.

4. *Heat of decomposition.* Detonation, effected in the calorimetric bomb, gave for one equivalent (= 284 grms.) + 116 Cal. at constant volume, which corresponds to the following decomposition :—

$$CHg(NO_2)CN = 2CO + N_2 + Hg,$$

or 114·5 Cal. at constant pressure, which for one grm. = 403 cal.

According to this equation, only carbon monoxide, nitrogen, and mercury vapour are formed. One only of these bodies is a compound; it is stable and not susceptible of dissociation, which accounts for the suddenness of the explosion. Moreover, the heat is disengaged at first, and all the gases are produced without the occurrence during cooling of any progressive recombination, which would tend to moderate the expansion and diminish the violence of the first shock.

The condensation of the mercury vapour, however, exercises an influence of this kind; but only after the principal cooling has lowered the temperature below 360°.

5. *Heat of formation from the elements.* From the above data we find that

$$C_2\text{(diamond)} + Hg + N_2 + O_2$$

absorbs + 51·6 − 114·5 = − 62·9 Cal. for 284 grms.

There is, therefore, absorption of heat in the formation of the fulminate—a property in concordance with the explosive character of the substance.

6. *Heat of total combustion.* Admitting the following reaction—

$$CHg(NO_2)CN + O_2 = 2CO_2 + Hg + N_2,$$

we shall get + 250·9 Cal. for one equivalent; or for one grm., 883 cal.

This combustion may be effected, in the case of primings, by mixing potassium chlorate with the fulminate, which causes the heat disengaged to amount to + 262·9 Cal. per equivalent. But in this instance we are heating 406·6 grms. of material instead of 284 grms; we get then for one grm., 647 cal.

We should also note the effects of expansion, due to the dissociation of the carbonic acid, which renders the mixture less sudden in its effects than pure fulminate.

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CHAPTER XI.

HEATS OF FORMATION OF THE CYANOGEN SERIES.

§ 1. Historical.

Few series of compounds in chemistry are of greater importance than that of cyanogen, owing to the nature of the compound radical that constitutes the characteristic pivot of the series. It is the only electro-negative radical that has, up to the present, been isolated. The exceptional properties of simple cyanides, with their resemblance to the salts of the halogen elements, and the still more singular properties of the double cyanides, add to the interest of the cyanogen series. Several of the compounds derived from it are employed in the manufacture of explosives.

In 1871, 1875, and finally in 1879 and 1881, the author devoted long courses of experiments to the thermal study of this series, which are published in the "Annals de Chimie et de Physique," 5e série, tom. v. p. 433; and tom. xxiii. pp. 178, 252.

These experiments, which were commenced during the spring and summer of 1871, partly at Versailles and partly at Paris, in the midst of the tumults of that year of trouble, presented great difficulties and even serious dangers, for it was necessary to use pure hydrocyanic acid and liquefied cyanogen chloride, which are the most poisonous substances known.

The calculation of the fundamental quantities is based principally on the measurements that were made of the heats of formation of cyanogen, hydrocyanic acid, potassium cyanate, and cyanogen chloride. The experiments on which the calculation of these quantities was based will be given in full. But various alterations have been made in the values deduced from them, principally on account of the complication caused in the calculations by the intervention of the heat of formation of ammonia. It has already been shown (pp. 237–242) to what degree the former estimates of this quantity were inaccurate, and the methods employed to rectify them. In 1882,

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M. Joannis completed the author's results, in the laboratory of the latter, by a prolonged study of various simple cyanides, ferrocyanides, ferricyanides, and sulphocyanides. His paper will be found in full, in the "Annales de Chimie et de Physique," 5e série, tom. xxvi. p. 482. The author's results concerning explosive substances have been given in table x., p. 132.

§ 2. Cyanogen.

1. The heat of formation of cyanogen has been measured in two ways—by ordinary combustion and by detonation. The following is the principle upon which the calculation is based. The heat of formation required depends on the heat of formation of carbonic acid, which is regarded as equal to 94 Cal. for

$$C\,(\text{diamond}) + O_2 = CO_2.$$

On subtracting twice this quantity from the heat of combustion of cyanogen, referred to the weight, which answers to the equation—

$$C_2N_2 + 2O_2 = 2CO_2 + N_2,$$

the difference represents the heat disengaged by the decomposition of the cyanogen. Consequently, this same difference taken with the opposite sign, expresses the heat absorbed in the combination of the carbon and nitrogen.

2. It is convenient to begin with ordinary combustion, by means of which the following results were obtained.

The combustion of cyanogen by pure oxygen is easily effected in the little glass combustion vessel shown on p. 241. With a suitable excess of oxygen there is no formation of carbon monoxide; so that we are at once enabled to deduce the weight of cyanogen consumed from the weight of carbonic acid which is formed and collected in a bulbed tube (into which is subsequently introduced a lump of solid potash).

This combustion, however, presents a complication owing to the formation of a little nitric peroxide. This body is absorbed by the potash, together with the carbonic acid; its weight should therefore be deducted. To do this, it is determined by consecutive operations. For example, assuming that the original nitric peroxide has, on contact with the potash, been converted into nitrous and nitric acids, we can then titrate the nitrous acid by means of potassium permanganate. The correction resulting from this is not of much importance; in the author's experiments it varied from one to three hundredths of the total weight of the carbonic acid. This correction involves another of still less importance, based on the fact that the formation of nitric peroxide from its elements causes an absorption of heat (– 2·6) which should be added to that

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obtained by the calorimeter; but this new addition is insignificant.

On calculation, the following values, referred to 26 grms. of cyanogen, were obtained :—

Weight of cyanogen consumed.						
·419	grm.	...	...	...	...	133·2 Cal.
·630	„	...	...	...	...	130·0 „
·574	„	...	...	...	...	131·3 „
·732	„	...	...	...	...	129·6 „
				Mean	...	131·6

i.e. for 52 grms. ($= C_2N_2$) + 263·2 Cal.

3. The author had also recourse to detonation in the calorimetric bomb (p. 148). In this way, the value + 261·8 was obtained. This result was obtained at constant volume, but it also applies to combustion at constant pressure; the combustion of cyanogen not giving rise to any change of volume.

It will be convenient to adopt the mean of the two results, viz. + 262·5 Cal. Thomsen, who has repeated these experiments quite recently, and after the publication of the above results, obtained + 261·3, which comes as near as can be expected.

Dulong had obtained in 1843 + 270 Cal.: the discrepancy in this value will not seem excessive, when we take into consideration to what perfection calorimetric methods have been brought since that time.

From results made, it follows that

$$C_2 \text{ (diamond)} + N_2 \text{ absorbs} - 74{\cdot}5.$$

If the carbon is supposed to be in the condition of charcoal, we should only get − 68·5. Thus cyanogen, CN, like acetylene, CH,[1] nitric oxide, NO, and all other substances acting as true compound radicals, is a body formed with absorption of heat; a circumstance to which attention has already been called more than once, as it seems calculated to account for the very character of this real compound radical, which manifests in its combinations an energy greater than that of its free elements. The energy of these latter is increased by this absorption of heat, instead of being weakened, as is the case in combinations that give off heat, and this increase of energy renders the compound system comparable to the more active elements.

§ 3. Hydrocyanic Acid.

1. The heat of formation of hydrocyanic acid is deduced by means of three methods, or series of independent measurements, the results of which agree.

[1] Acetylene and cyanogen are here considered under the same volume as the simple radicals H and Cl.

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The author first took, in 1871, as his starting-point—

(*a*) The conversion of hydrocyanic acid into formic acid and ammonia.

(*b*) The conversion of mercuric cyanide by gaseous chlorine and alkalis into carbonic acid, hydrochloric acid, mercuric chloride, and ammonium chloride.

These two methods are based upon the employment of the wet process. They require the knowledge of a great many auxiliary data, and especially of the heat of formation of ammonia. Now, the heat of formation of ammonia as adopted in the first calculations, according to Thomsen's measurements, which were then universally accepted, was reputed to be equal to + 35·15 (NH_3 in solution). As this number should be reduced to + 21, according to later conclusions (p. 242), the correctness of which Thomsen has himself acknowledged, it became necessary to deduct the difference between these two values, *i.e.* 14·15, from the heat of formation (from the elements) of hydrocyanic acid and also from that of cyanides. But it was thought necessary to check this correction by measuring the heat of formation of hydrocyanic acid by means of experiments of another order, which are quite independent of the heat of formation of ammonia, and in which the number of auxiliary data was as limited as possible.

(*c*) This purpose was effected by burning a mixture of hydrocyanic acid gas and oxygen by detonation in the calorimetric bomb—

$$2HCN + 5O = 2CO_2 + N_2 + H_2O.$$

Three data only are required in this case, viz. the heats of combustion of carbon, hydrogen, and hydrocyanic acid. The experiments made according to this method will be described first.

2. First Method.—*Combustion of hydrocyanic acid.* Pure liquid hydrocyanic acid is introduced, by distillation, into little phials of thin glass, care being taken to keep the weight of the acid within suitable limits (·14 to ·15 of a gramme in these experiments). These limits are regulated by the capacity of the calorimetric bomb, the tension of hydrocyanic acid vapour at the temperature of the experiment, and the necessity of introducing into the bomb a sufficient amount of oxygen to obtain total combustion. The tension of hydrocyanic gas being about ·59 of a metre at 18°, *i.e.* almost three-quarters that of the atmosphere, it is easy to fulfil the conditions required.

The phial, sealed up and weighed, furnishes the exact weight of hydrocyanic acid. This phial is carefully placed in the bomb, which is then closed, and filled, by means of an orifice, with pure dry oxygen at a suitable pressure. The orifice is then carefully closed, and the phial containing the hydrocyanic

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acid broken to pieces by being violently shaken. The acid is thus wholly converted into gas and constitutes with the oxygen a detonating mixture.

This being done, the bomb is placed in the calorimeter, and thermal equilibrium established; we note the progress of the thermometer and then proceed to detonate the mixture. After the detonation, we again follow the progress of the thermometer. The gas is then extracted by means of a mercury pump, and caused to pass first through a drying apparatus, and then through tubes containing potash. The bomb is then purified by filling it several times with dry air, which is also passed through the same tubes, so as to extract the whole of the carbonic acid.

This can thus be weighed, which affords a valuable check on the combustion.

Special trials showed that the quantity of nitrous compounds formed in the combustion was negligable, but that a trace of hydrocyanic acid always escaped. The latter was determined each time in the potash, after the weighing; it amounted to between half a hundredth and a hundredth of the original weight. This was taken into account.

These points having been settled, the heat disengaged was calculated in two ways; either by considering it in relation to the weight of hydrocyanic acid employed (minus the trace which is not oxidised), or to the weight of carbonic acid obtained (with the same deduction). The list of results observed may be given. The heat absorbed, owing to the tension of the aqueous vapour in the bomb at the temperature of the experiment, was taken into account; also + 0·4 was added to all the results obtained, in order to allow for the fact that the detonation was effected at constant volume. The heats of combustion given below are supposed to be obtained at constant pressure. We will now give the heat disengaged by the combustion of 27 grms. of gaseous hydrocyanic acid (HCN = 27 grms.), effected by means of free oxygen at constant pressure.

According to the final weight of the hydrocyanic acid.	According to the initial weight of the carbonic acid.
158·9	163·4
160·0	161·3
154·2	155·6
159·0	160·4
160·1	160·3
Mean ... 158·4	Mean ... 160·2

The general mean, 159·3, of the two calculations will be adopted. Thomsen, according to results which he published after those just given, obtained by ordinary combustion + 159·5, a value agreeing with that of the author as closely as could be expected.

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It is a fact worthy of mention that this number exceeds the united heats of combustion of the carbon and hydrogen contained in the hydrocyanic acid, whatever form the carbon may be in.

C (diamond) $+ O_2 = CO_2$	$+ 94$ (charcoal)	$+ 97$
$\frac{1}{2}[H_2 + O = H_2O$ (liquid)]	$+ 34{\cdot}5$ „	$+ 34{\cdot}5$
	$+ 128{\cdot}5$	$+ 131{\cdot}5$

According to these figures and this method, the formation of hydrocyanic gas from its elements, $H + C + N = HCN$, absorbs $+ 128{\cdot}5 - 159{\cdot}3 = - 30{\cdot}2$ when the carbon is in the form of diamond, and $- 27{\cdot}2$ when it is in the form of charcoal.

3. Second Method.—*Conversion of the hydrocyanic acid into formic acid and ammonia.* This change is effected by means of concentrated hydrochloric acid. In addition to the data concerned in the direct experiment we must also have the heat of formation of ammonia, the heat of combination of this base with hydrochloric acid, the heat of dilution of hydrochloric acid, and, lastly, the heat of combustion of formic acid, carbon, and hydrogen, so that we have, in all, six auxiliary data.

A known weight of pure hydrocyanic acid was decomposed in the calorimeter by means of very concentrated hydrochloric acid. When the change was effected, it was proved to be complete or practically so; the mixture was diluted with a large quantity of water, and the new quantity of heat evolved measured. In a similar way was measured the heat disengaged by the mixing of the same quantities of concentrated hydrochloric acid and water.

From this was deduced the quantity of heat that would be disengaged by the following reaction:—

HCN (pure and liquid) $+ HCl$ (diluted) $+ 2H_2O = H_2CO_2$ (in solution) $+ NH_4Cl$ (in solution); or $+ 11{\cdot}15$ Cal.

Experiments.—Some details of one of the experiments taken as a type may now be given.

Preliminary operations.—The calorimeter contains 500 cms. of water. It is placed in a double enclosure, in the centre of a quantity of water, the temperature of which is exactly the same, *i.e.* to within 0·1 of a degree, as that of the water in the calorimeter, and that of the room in which the experiment is being performed. This point is essential.

In the centre of the calorimeter is placed a little cylinder of thin platinum, of a capacity of about 50 cms., with no opening at the base, and closed at the top by means of a cork coated with paraffin. This cylinder floats in the water of the calorimeter, in which it is immersed nearly up to its top. We first introduce into it 35 grms. of hydrochloric acid, which is concen-

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trated but not saturated; then we place in the same cylinder a glass phial containing 1·591 grm. of absolutely pure hydrocyanic acid—the phial itself weighs 1·568 grm.—it is very thin and elongated into a point at each end, so as to be easily broken when the cylinder is shaken.

These operations having been quickly performed, and the phial being sealed, the cylinder is corked up, and the calorimetric thermometer observed during an interval of ten minutes. There was absolutely no variation during this interval in the experiment performed. The temperature was about 20°.

First stage.—After the preliminary operations, we raise the platinum cylinder a little by means of a pair of wooden pincers, without, however, drawing it entirely out of the water, and shake it violently so as to break the phial. It is then plunged immediately into the calorimeter, and the course of the thermometer again observed at the end of each minute. Reaction takes place, and the heat given off is gradually absorbed by the water of the calorimeter. The variation of temperature is most rapid at the commencement, but the maximum temperature is not produced until after a considerable length of time. It exceeds the original by + 1·3°. It lasts for a quarter of an hour and then the temperature slowly falls. We follow this cooling for forty minutes, during which interval it only amounts to 0·17 of a degree. This is the first stage of the experiment.

Second stage.—We next incline the platinum cylinder and open it under the water of the calorimeter, so as to fill it; the contents of the cylinder are mixed with those of the calorimeter by stirring, until the thermometer, on being plunged alternately into the calorimeter and cylinder, indicates exactly the same temperature. This is the second stage of the operation. It lasts about a minute, and gives rise to an excess of + 1·5° over the temperature of the calorimeter at the beginning of this stage, or + 2·6° over the temperature at the beginning of the entire experiment, *i.e.* at the beginning of the first stage. The rate of cooling during an interval of five minutes is then observed and the experiment is ended.

Verifications.—We then make sure, by means of suitable reactions (the formation of Prussian blue), that the liquid contains no appreciable quantity of hydrocyanic acid—the latter having been entirely converted into formic acid and ammonium chloride.

Moreover, in order to calculate the rate of cooling during the first stage of the experiment, we proceed, by the addition or subtraction of suitable quantities of water, to bring the temperature of the liquid contained in the calorimeter (the mass of water being kept constant during these fresh mixtures) to + 1·3° above that of the enclosing vessel and

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surrounding atmosphere, which should not vary to any appreciable extent during the whole course of the experiment. We then follow for half an hour the rate of cooling, which corresponds to this fresh increase of temperature, the conditions observed being, as nearly as possible, the same as those of the first stage.

The above experiment gave—

Initial temperature of the calorimeter	...	+ 19·82
Initial temperature of the enclosing vessel	...	+ 19·98
Final temperature of the enclosing vessel	...	+ 20·06

Calculation from the experiment.—We now have to calculate the actual quantity of heat disengaged during this experiment. It is obtained, as we know, by multiplying the masses employed, reduced to units of water by the variation of temperature observed, this variation increasing with the lowering of temperature produced during cooling.

Masses reduced to units of water.—Of the substance employed, the mass existing at the end of the experiment consists of that in the water, which contains about $\frac{1}{100}$ its weight of hydrochloric acid, $\frac{1}{2000}$ of ammonium chloride, and about as much formic acid. Their weight being known from the original data, the density is next taken, and then the volume calculated. We assume that 1 cc. of this liquid absorbs 1 cal. for a rise in temperature of 1°, an hypothesis sufficiently near the truth for calculations of this kind.[1]

We reduce to units of water the various vessels of platinum and glass that are used, and also the thermometer (that is, the portion submerged), multiplying the weight of each vessel or portion of vessel by its specific heat. The sum of all these masses represents the total mass that has been subjected to the variation of temperature observed.

The actual variation of temperature is the apparent variation plus that corresponding to the heat lost during the first and second stages of the experiment.

The calculation of these quantities will now be given, and first of all, that during the second stage, as it is the easiest.

Heat lost during the second stage.—This is easily calculated, for the duration of the second stage is only one minute, with a final excess of temperature of 2·5° above that of the enclosing vessel. In fact, the loss of heat during the few following minutes was measured and found to be almost uniform. We calculate from this the mean loss during one minute; then we multiply the quantity thus got by the fraction $\frac{4}{5}$, for we assume that the excess of temperature in the calorimeter, which varied from 1·5° to 2·6° during one minute, has caused a loss

[1] "Annales de Chimie et de Physique," 4ᵉ série, tom. xxix. p. 163.

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equal to that which would have resulted for a mean excess of $\frac{1{\cdot}5 + 2{\cdot}6}{2} = 2°$.

The resulting correction is very insignificant; it only amounted to 0·02 of a degree in 1·5°.

We then calculate the total heat, Q_1, disengaged during the second stage by multiplying the sum of the masses, reduced to units of water, by the apparent variation of temperature, added to that corresponding to the heat lost.

Heat lost during the first stage.—The loss of heat during the first stage requires a more complicated mode of calculation. This first stage is divided into periods of at least five minutes, according to the rapidity of the heating, until the maximum temperature is attained. The mean temperature of each period is written down, and also the excess of this mean temperature over the initial temperature.

The duration of the maximum temperature constitutes a separate period, corresponding to the maximum excess of temperature.

The time following this maximum is also divided into periods of five minutes, and opposite each period are written the mean temperature and the excess of temperature.

At the end of this time it was observed that the rapidity of cooling was, for the same excess of temperature over the initial temperature, exactly the same as in a check experiment made a little later, and in which care was taken to reproduce this excess under the same conditions.

This verification proves that the reaction was quite complete, and that the data of the check experiment may be applied to the calculation of losses of heat during the reaction itself.

In fact, this check experiment gives, without any hypothesis, the losses of heat experienced by the calorimeter for a series of excesses of temperature similar to those of the reaction, and under conditions exactly parallel.

We then write down the loss of heat experienced by the system in one minute for each mean excess of temperature answering to each period; we multiply this loss by the duration of the period, generally five minutes (except in the case of the maximum, which is longer). We then find the sum of all these losses, and add them to the variation of temperature actually observed.

To come to figures, it may be said that, the variation observed being + 1·26°, the correction was + 0·234°, which will not seem too great in an experiment of such long duration.

We have now only to multiply the corrected variation of temperature by the sum of the heated masses (reduced to units of water), in order to obtain the quantity of heat, Q_2, disengaged. It is advisable to give these details, because they afford as

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exact an idea as possible of experiments of this kind, and of the difficulties which they present. Of course, we could not expect the same degree of accuracy as in experiments of short duration, but, nevertheless, the errors can hardly exceed ·05 of the total value.

4. *Calculation from the theoretical reaction.* It now remains for us to deduce from the numbers observed the values which are applicable to the reaction taken from a theoretical point of view. For this purpose, the same weight is taken of the same solution of concentrated hydrochloric acid, viz. 35 grms. (or a weight very near to this, in which case the results are afterwards referred to this weight by proportional calculation); it is dissolved in the same quantity (500 cc.) of water at the same temperature; then the heat, Q_3, disengaged is measured.

This quantity being known, the difference, $Q_1 + Q_2 - Q_3$, represents exactly the heat disengaged by the conversion of the weight employed of pure hydrocyanic acid by means of hydrochloric acid (diluted), into formic acid (diluted), and ammonium chloride (diluted), as the initial state and the final state are absolutely identical. Multiplying this quantity by the ratio of the equivalent (HCN = 27 grms.) to the weight of hydrocyanic acid actually employed, we obtain the heat disengaged in the theoretical reaction—

$$\text{HCN (pure and liquid)} + \text{HCl (diluted)} + 2H_2O = H_2CO_2 \text{ (diluted)} + NH_4Cl \text{ (diluted)}.$$

The following numbers were found by experiment, + 11·54 and + 10·76, or, on an average, + 11·15.

5. From this is deduced *the heat of formation of hydrocyanic acid from its elements, carbon (diamond), gaseous hydrogen, and gaseous nitrogen*—

$$H + C + N = HCN \text{ (pure and liquid)}, \text{ absorbs } - 22{\cdot}6.$$

In short, supposing the initial system to be

$$5H + C + N + O_2 + HCl \text{ (diluted)},$$

and the final system

$$H_2CO_2 \text{ (diluted)} + NH_4Cl \text{ (diluted)},$$

we pass from one to the other by two different processes.

FIRST STEP.

$H_2 + C + O_2 = H_2CO_2$ (pure) disengages	+ 93·00
H_2CO_2 (pure) and water	+ 0·10
$N + H_3 = NH_3$ (in solution)	+ 21·00
NH_3 (diluted) + HCl (diluted) = NH_4Cl (diluted) ...	+ 12·45
Sum ...	+ 126·55

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SECOND STEP.

$2(H_2 + O) = 2H_2O$	+ 138·00
$H + C + N = HCN$ (pure and liquid)	x
Reaction of HCl (diluted)	+ 11·15
Sum ...	+ 149·15

Thus,

$$x = -149{\cdot}15 + 126{\cdot}55 = -22{\cdot}6.$$

This value applies to liquid hydrocyanic acid.

6. *Vaporisation of hydrocyanic acid.* In order to pass to the gaseous state of the acid, we must determine the heat absorbed in its vaporisation. To do this, the following method was adopted, which may be applied to all liquids of similar volatility. It consists in vaporising them in a current of dry gas and measuring the heat absorbed. We pour into a glass phial a known weight, say 1·396 grm., of pure hydrocyanic acid; we then seal up the phial, which should be thin and provided with two points easily broken. This is introduced into a little glass receiver, fitted with a worm and arranged so that a regular current of air may be made to circulate in it by means of an aspirator, the gaseous current first passing through the recipient and then through the worm.

This little system is plunged into the calorimeter, which contains 500 grms. of water. It is immersed almost up to the orifice of the receiver, which is closed by a cork through which a tube is passed, by means of which the current of air may pass.

This air is perfectly dry, and its temperature during its passage is shown by a thermometer indicating twentieths of a degree; the volume of this air is determined sufficiently accurately for the calculation into which it enters, by measuring the volume of water that has flowed from the aspirator. It may be added that a solution of alkali was placed between the worm and the aspirator in order to absorb the hydrocyanic gas, and thereby prevent its noxious fumes. These preparations having been made, the phial being still closed, a certain volume of air is allowed to circulate for twenty minutes through the receiver and worm, in order to estimate the cooling. The experiment for which the results are given gave a value of 0 for the initial cooling. This result is easily explained, as the temperature of the water in the calorimeter was + 20·07, that of the water of the enclosing vessel, + 20·22, and that of the surrounding air, + 20·8.

The phial is then broken against the sides of the receiver by the violent shaking of the latter. The gaseous current is allowed to continue circulating, and the thermometer is read. The experiment lasts twenty minutes, during which the liquid acid has entirely disappeared, and the minimum temperature is reached almost immediately. This minimum corresponds to a

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fall of temperature of − 0·510°. The circulation of the gaseous current is continued for twenty minutes longer, in order to measure the re-heating, which, under these conditions, is very slight.

We then possess all the data necessary for calculating the heat of vaporisation of hydrocyanic acid under the conditions described above.

It was found—

For HCN = 27 grms. (1st trial)...	...	5·680
For HCN = 27 grms. (2nd trial)	...	5·730
Mean	...	5·705

Thus *the formation of gaseous hydrocyanic acid from its elements*, according to this method—

$$H + C \text{ (diamond)} + N = HCN \text{ (gas)}, \text{ absorbs } - 28{\cdot}3.$$

7. *Solution of hydrocyanic acid.* The solution of the liquid acid in water may give rise to either a disengagement or to an absorption of heat, according to the relative proportions, and also to the temperature if the proportion of water be small.[1]

In this case only the heat disengaged in the presence of a large quantity of water was measured. It was found that

$$HCN \text{ (liquid)} + 60H_2O, \text{ at } 19°, \text{ disengages } + 0{\cdot}40.$$

8. Third Method.—*Conversion of mercuric cyanide into mercuric chloride, carbonic acid, and ammonia.* This method consists in dissolving gaseous chlorine in water contained in a closed calorimeter, weighing it, and treating the solution obtained with an exactly equivalent weight of mercuric cyanide; the latter becomes converted into mercuric chloride and cyanogen chloride (in solution)—

$$\tfrac{1}{2}[2Cl_2 \text{ (in solution)} + Hg(CN)_2 \text{ (in solution)} = HgCl_2 \text{ (in solution)} + 2CNCl \text{ (in solution)}].$$

The quantity of water to be employed must be calculated, so as to be much greater than would be necessary to hold in solution the whole of the carbonic acid finally formed. We then add diluted potash, in proportions equivalent to the chlorine, so as to obtain potassium chloride and potassium cyanate—

$$CNCl \text{ (in solution)} + K_2O \text{ (diluted)} = KCNO \text{ (in solution)} + KCl \text{ (diluted)}.$$

Without troubling ourselves whether the action is more or less complete, we immediately pour an excess of diluted hydrochloric acid into the same calorimeter, so as to bring the whole

[1] Bussy and Buignet, "Annales de Chimie et de Physique," 4e série, tom. iii. p. 235.

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mass to the final state of carbonic acid (in solution), ammonium chloride (in solution), potassium chloride, and mercuric chloride (in solution). We thus get—

$$KCNO\ (diluted) + HCl\ (diluted) + H_2O = CO_2\ (in\ solution) + NH_3\ (diluted) + KCl\ (diluted).$$

We measure the total heat disengaged in this series of reactions; the whole series occupying a period not exceeding from twenty to twenty-five minutes. Then we make sure that there is no cyanogen compound remaining in solution; this is confirmed by the quantitative estimation of the ammonia, made in the cold by the Schloesing process.

The total heat disengaged by this series of reactions being known, the following data are brought into the calculation—the heats of combustion of carbon and hydrogen, the heat of oxidation of mercury, the heat of chlorination of hydrogen, the heat of formation of ammonia, the heats of combination of mercuric oxide with hydrochloric and hydrocyanic acids, and lastly, the heats of combination of diluted potash and dissolved ammonia with hydrochloric acid; making in all, nine auxiliary data.

In short, we proceed from the initial state, which is—

$$\tfrac{1}{2}[C_2 + N_2 + 4H_2 + Hg + 2Cl_2 + 2O_2 + 2K_2O\ (diluted) + 4HCl\ (diluted)],$$

to the final state—

$$\tfrac{1}{2}[2CO_2\ (in\ solution) + 2NH_4Cl\ (diluted) + 2H_2O + 4KCl\ (diluted) + HgCl_2\ (diluted)].$$

By one mode of procedure, the compounds of the final state may be formed directly; the heat of formation of mercuric chloride in particular being determined from the heats of formation of water, mercuric oxide, and hydrochloric acid, together with the heat disengaged by the solution of the oxide in this acid.

By a second method, the diluted hydrocyanic acid and mercuric oxide are formed first, and then combine.

H + C + N (liquid) disengages	x
HCN (liquid) and water	+ 0·4
$\tfrac{1}{2}[Hg + O = HgO]$	+ 15·5
$\tfrac{1}{2}[HgO + 2HCN\ (diluted) = Hg(CN)_2\ (diluted) + H_2O]$	+ 15.46

We then add to this sum the total amount of heat disengaged in the calorimeter during the course of the operations, without troubling about the chemical nature of the intermediate reactions.

The details of the experiments will not be given here, as they will be found further on, under cyanogen chloride. It will merely be remarked that the quantity, x, calculated from

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experiments of this order and from the value at present adopted for the formation of ammonia (p. 242), was found to be equal to − 24·3. This relates to liquid hydrocyanic acid. We get then, according to this method—

$$H + C + N = HCN\ (gas) - 30.$$

9. In short, the following numbers have been obtained for the formation of hydrocyanic gas—

By the first method (detonation)	− 30·2
By the second method (formic acid and ammonia) ...	− 28·3
By the third method (mercuric cyanide and chlorine) ...	− 30·0
Mean ...	− 29·5

This mean value will be adopted to express the heat absorbed by the combination of the elements—

H + C (diamond) + N = HCN (gas)	− 29·5 Cal.
HCN (liquid), we should get	− 23·8 „
HCN (in solution)	− 23·4 „

10. From these figures it follows that cyanogen and hydrocyanic acid are both formed from their elements with absorption of heat. This circumstance explains, as has already been said, the character of cyanogen as a compound radical, and, in a more general manner, the tendency of cyanogen and hydrocyanic acid to form direct combinations and polymeric compounds, and to give rise to complex reactions. The fresh determinations which are here published confirm the views which were expressed by the author on this subject twenty years ago, with regard to cyanogen, acetylene, and endothermal combinations.[1]

11. It will be remembered that cyanogen, hydrocyanic acid, acetylene, etc., may be regarded as following the general rule applicable to chemical compounds, *i.e.* as being formed with disengagement of heat; if we assume that the carbon, when under the form of diamond or charcoal, does not correspond to true elementary carbon, the latter would be comparable to hydrogen, and would probably be in the gaseous state, charcoal and diamond representing its polymeric forms. In passing from the gaseous to the polymeric and condensed state, the elementary carbon would give off a considerable quantity of heat, which is greater than that absorbed in the formations of acetylene (− 30·5 for C = 12) and cyanogen (− 37·3).

The quantity of heat developed by the condensation of the elementary carbon might even be estimated at + 42·6 for diamond and + 39·6 for charcoal, if we assume that the successive formation from the gaseous carbon of the products of the two

[1] "Annales de Chimie et de Physique," 4e série, tom. vi. pp. 351 et 433.

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degrees of oxidation of carbon, viz. carbon monoxide and carbonic acid, gives off the same quantity of heat. These are conjectures of some interest, and have been accepted by various savants since they were first broached.[1]

12. However this may be, the figures actually obtained lead us to conceive a very definite opinion, which is confirmed by experiment. In fact, they show that the formation of hydrocyanic gas from cyanogen and hydrogen—

$$H + CN = HCN, \text{ gives off } + 7{\cdot}8 \text{ Cal.}$$

This formation is therefore exothermal; a circumstance which led to the suspicion that it might be effected directly, notwithstanding the negative experiments that had been made previously by Gay-Lussac. In fact, the direct combination of the two gases was effected directly by means of time and heat alone, and under conditions comparable with those in the synthesis of the hydracids of the halogen elements properly so called.[2]

13. The synthesis of gaseous hydrocyanic acid from acetylene and free nitrogen, a synthesis very easy to effect through the action of the electric spark, as was discovered in 1868—

$$C_2H_2 + N_2 = 2HCN, \text{ disengages } + 2{\cdot}1 \text{ Cal.},$$

a positive though very low quantity.

14. As to the formation of hydrocyanic acid from ammonium formate and formamide, which is the simplest type of a general reaction in organic chemistry, viz. that for the formation of nitrils, it is worthy of special attention.

Let the reaction be as follows:—

$$NH_4CHO_2 = HCN + 2H_2O,$$

the water and the acid being supposed to be separate.

This reaction, if it could be effected with solid bodies at the ordinary temperature, so as to produce water and liquid hydrocyanic acid, would absorb − 13·7 Cal. Effected with the dissolved salt, it would absorb − 10·4 Cal.

Let us again note the initial system—

$$H_2CO_2 \text{ (pure)}, NH_3 \text{ (diluted)}, HCl \text{ (diluted)};$$

and the final system—

$$HCN \text{ (pure)}, HCl \text{ (diluted)}, 2H_2O.$$

We may pass from one to the other by two different methods.

[1] "Annales de Chimie et de Physique," 4ᵉ série, tom. xviii. pp. 161, 173, and especially 175.

[2] Ibid., 5ᵉ série, tom. xviii. p. 378. The heat of formation of hydrocyanic acid, admitted in the article quoted, was estimated, by means of the data then known, at + 26·9; this is too high, but the sign of the phenomenon remains the same, and, consequently, the preconceived idea of its being synthetic.

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First Step.

H_2CO_2 (pure) + water	+ 0·08
H_2CO_2 (diluted) + NH_3 (diluted)	+ 12·0
Separation of solid ammonium formate	+ 2·9
NH_4CHO_2 (solid) = HCN (liquid) + $2H_2O$ (liquid) ...	+ x
HCl (diluted) no change.	
Sum ...	+ 15·0 + x

Second Step.

NH_3 (diluted) + HCl (diluted)	+ 12·4
H_2CO_2 (pure) + water	+ 0·08
NH_4Cl (diluted) + H_2CO_2 (in solution) = HCN (liquid) + HCl (diluted) + $2H_2O$	− 11·15
Sum ...	+ 1·3

$$x = -15 + 1{\cdot}3 = -13{\cdot}7 \text{ Cal.}$$

In fact, the salt, when melted, is really destroyed, with the production of water and hydrocyanic acid, both in a gaseous form; it thus absorbs, besides the − 13·7 Cal. mentioned above, the heat necessary for the vaporization of these two substances, *i.e.* a value approximately[1] = − (5·7 + 19·3) + F, where F is the heat of fusion of the salt. This gives then − 38·7 + F, which amounts to about − 36 Cal.

A similar absorption would no doubt be produced if the ammonium formate could exist in a gaseous form and be decomposed as such.

In short, the formation of formonitril from ammonium formate absorbs, whatever hypothesis is adopted, a great quantity of heat; a result in accordance with what happens in most decompositions.

We may go further than this. In fact, the dehydration of ammonium formate is effected by two stages, formamide and water being first produced—

$$NH_4CHO_2 = CNH_3O + H_2O.$$

The liquid formamide was acted upon by means of concentrated hydrochloric acid, so as to give the opposite reaction. From the numbers observed it was deduced that the theoretical reaction, *i.e.* in the case of the use of diluted acid, would give off + 1·4 Cal., a value which is probably too low, and is given here with some diffidence, as the formamide, being in the liquid state, cannot be guaranteed pure. It is practically applicable to the change of formamide (in solution) into ammonium formate (in solution), the value deduced being + 1.

We conclude, from these figures, that the decomposition of the melted ammonium formate into gaseous formamide and

[1] The term *approximately* is used, because the heats of vaporisation of the bodies concerned in the experiment at the temperature of decomposition of ammonium formate (180° to 200°) are not the same as at the boiling points.

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steam will absorb about + 18 Cal. (supposing the vaporisation of the formamide to absorb from 6 to 8 Cal.).

The two stages of the dehydration of crystallised ammonium formate, which is changed first into gaseous amide and then into gaseous nitril, would correspond to thermal phenomena that may be considered as having equal effects, the first stage absorbing − 18 Cal., and the two stages together − 36 Cal. But this equality would only exist when the products are considered in the gaseous state.

Conversely, the fixing of the elements of water, either upon the formamide or upon the formonitril (in solution), so as to reproduce the ammonium salt (in solution), gives off a quantity + 1 Cal. for the amide, and + 10·4 for the nitril; quantities which are very unequal but both positive.

This is another proof of the disengagements of heat which may result from simple hydration effected by the wet process, and especially so from that of amides, which play a very important part in the study of the reactions of organic nitrogenous principles, and that of animal heat.[1]

The formation of cyanides will now be explained.

§ 4. Potassium Cyanide.

1. It was found, by experiment, that at about 20°—

	Cal.
HCN (liquid), on being dissolved in 40 times its weight of water, gives off	+ 0·40
½[2HCN (diluted) + K_2O (diluted)]	+ 2·96
KCN (pure), on being dissolved in 50 times its weight of water, absorbs	− 2·86

From this we deduce the heat disengaged by the formation of solid potassium cyanide from the elements—

$$K + C + N = KCN \text{ (crystalline) disengages } + 30{\cdot}3$$

The calculation is as follows:—

Initial system; ½[K_2 + C_2 + N_2 + H_2 + O].
Final system; ½[2KCN (crystal.) + H_2O (liquid and separate)].

First Step.

H + C + N = HCN (liquid) absorbs	− 23·8
HCN + *n*Aq	+ 0·4
½[K_2 + O + *n*Aq = K_2O (diluted)]	+ 82·3
½[2HCN (in solution) + K_2O (in solution) = 2KCN (in solution) + H_2O]	+ 3·0
Separation of KCN (solid)	+ 2·9
Sum ...	+ 64·8

[1] "Annales de Chimie et de Physique," 4ᵉ série, tom. vi. p. 461.

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SECOND STEP.

$K + C + N = KCN$ (crystalline)	x
$\frac{1}{2}[H_2 + O = H_2O$ (liquid)]	$+ 34{\cdot}5$
Sum ...	$+ 34{\cdot}5 + x$

$$x = + 64{\cdot}8 - 34{\cdot}5 = + 30{\cdot}3.$$

2. The direct formation of potassium cyanide from the union of its elements, as expressed by chemical equation, and the corresponding disengagement of heat, is not really effected at the ordinary temperature. But it is admitted that it does actually take place at a very high temperature, when free nitrogen is made to act upon charcoal impregnated with potassium carbonate; *i.e.* under conditions where potassium is generated. At this temperature, the potassium cyanide is melted or perhaps even gaseous, a change of state which causes an absorption of heat; but, on the other hand, the potassium is gaseous, which compensates this absorption. If free nitrogen, carbon, and potassium do really combine without any other intermediate reaction, such as the formation of an acetylide (this formation has not been proved to take place), we should be led to admit that the total synthesis of potassium cyanide disengages heat, under the actual conditions of the reaction.

Be the disengagement produced at once or by successive reactions, it does not explain the total synthesis.

3. We come now to a clearer synthesis. The union of cyanogen with potassium takes place, as we know, directly. This union, calculated for the following states of the substances concerned—

K (solid) + CN (gas) = KCN (crystallised), disengages + 67·6 Cal.

These figures justify the direct synthesis of potassium cyanide from cyanogen. But this quantity is lower than that disengaged by the union of the same metal, in the solid state, with halogen elements in the gaseous state.

Now,

Cl + K = KCl (solid) gives off	+ 105·6
Br (gas) + K = KBr gives off	+ 100·4
I (solid) + K = KI gives off	+ 85·4

This difference explains why chlorine, bromine, and iodine decompose potassium cyanide in solution; cyanogen is liberated and combines, besides, with half the halogen, causing a slight additional disengagement of heat—

[+ 1·6 for CNCl (gas); + 4·2 for CNI (solid).]

4. It may also be mentioned, in order to complete this parallel, that the formation of potassium cyanide from the hydracid (diluted) and potash—

HCN (diluted) + KHO (diluted) = KCN (in solution) + H_2O,

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disengages much less heat (+ 3·0) than the formation of the chloride, bromide, and iodide of potassium under the same conditions (which disengages 13·7).

This difference would be increased by 17 Cal., if the hydrochloric and hydrocyanic acids were considered in the gaseous state.

Hydrocyanic acid is therefore much less powerful than the hydracids derived from halogen elements; it is even displaced in potassium cyanide in solution by most acids.[1] This inertness of hydrocyanic acid itself contrasts with the greater energy of the complex acids which it forms when associated with metallic cyanides; hydroferrocyanic acid, for example; this will be referred to later on.

5. The conversion of potassium cyanide into formate—

$$KCN \text{ (in solution)} + 2H_2O = KCHO_2 \text{(in solution)} + NH_3 \text{ (in solution), gives off} + 9{\cdot}5 \text{ Cal.}$$

This reaction does take place in solutions of the cyanide, although slowly.

The same reaction, effected on the dry salt by means of aqueous vapour, produces formate and ammonia gas; it is much more rapid, but gives off double the amount of heat: − 17·7.

If the temperature is raised, the reaction becomes complicated, owing to the ultimate destruction of the formate by the heat or excess of alkali; this reaction, which takes place at about 300° and finally transforms the potassium cyanide into potassium carbonate—

$$KCN \text{ (solid)} + KHO \text{ (solid)} + 2H_2O \text{ (gas)} = K_2CO_3 \text{ (solid)} + NH_3 \text{ (gas), gives off} + 37{\cdot}4.$$

This point is important, because it is one of the most effective causes of the destruction of potassium cyanide during its industrial preparation; in this case the melted salts are operated upon, and this fact causes a slight modification of the above values; without, however, altering their general signification. When exposed to the oxygen of the air, we know that potassium cyanide is readily converted into potassium cyanate. This reaction will be referred to at a later period.

§ 5. Ammonium Cyanide.

1. It was found that the combination of hydrocyanic acid in solution, with ammonia in solution, gives off + 1·3 Cal. The solution of freshly prepared ammonium cyanide (1 part of salt to 180 parts water) absorbs − 4·36 for NH_4CN (= 44 grms.).

2. From these figures it follows that the union of hydrocyanic gas and ammonia gas, with formation of solid cyanide—

$$HCN \text{ (gas)} + NH_3 \text{ (gas)} = NH_4CN, \text{ gives off} + 20{\cdot}5.$$

[1] "Annales de Chimie et de Physique," 4ᵉ série, tom. xxx. p. 492.

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This is only half the heat disengaged in the similar formations of chloride (+ 42·5), bromide, and iodide of ammonium;[1] the acetate comes nearer (+ 28·2), and the hydrosulphide nearer still (+ 23).

3. Starting from the elements, we should get—

$N_2 + C + 2H_2 = NH_4CN$ (solid) gives off + 40·5 Cal.

The analogous formation of ammonium chloride gives off + 76·7.

4. Lastly, the heat of formation of ammonium chloride from the elements is less than that of potassium chloride by 28·3 Cal.; whereas, between the formation of ammonium cyanide and that of potassium cyanide, the thermal difference is 27·1. The difference in the two cases is therefore almost the same; *i.e.* this state does not depend on the halogen generator.

§ 6. Metallic Cyanides.

1. It was found that gaseous cyanogen combines directly, not only with potassium, but also with certain true metals, such as iron, zinc, cadmium, lead, and even copper; but this tendency towards direct combination does not extend to mercury and silver.

2. The reactions are effected by heating cyanogen and the metals in sealed tubes, to 100° for the first-named metals, and to about 300° for the two last.

3. Such combinations are always attended by a disengagement of heat. In particular, according to M. Joannis—

$\frac{1}{2}[Zn + (CN)_2 = Zn(CN)_2]$ gives off + 28·5.
$\frac{1}{2}[Cd + (CN)_2 = Cd(CN)_2]$ gives off + 19·8.

From the elements, on the contrary—

$\frac{1}{2}[Zn + C_2 + N_2 = Zn(CN)_2]$ absorbs − 8·8.
$\frac{1}{2}[Cd + C_2 - N_2 = Cd(CN)_2]$ absorbs − 17·5.

§ 7. Mercuric Cyanide.

1. *Formation from the acid and the oxide.* It was found, by experiment, that dilute hydrocyanic acid and mercuric oxide—

$\frac{1}{2}$[2HCN (1 equiv. = 2 litres) + HgO (precipitated and diluted with 10 litres of water)], gives off + 15·48.

An excess of hydrocyanic acid does not cause any alteration in this value, which is considerable, exceeding even the heat given off in the action of dissolved hydrochloric acid on potash.

It is owing to this difference in values that potash, combined with hydrocyanic acid, with which, moreover, it gives off much

[1] See p. 127.

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less heat (3·0), is displaced by mercuric oxide. On the other hand, the solution of this salt—

$$\tfrac{1}{2}[Hg(CN)_2\,(solid) + water\ (1\ to\ 40)] - 1{\cdot}5\ ;$$

consequently,

$\tfrac{1}{2}$[2HCN (in solution) + HgO = $Hg(CN)_2$ (solid)] ... + 17·0
$\tfrac{1}{2}$[2HCN (liquid and pure) + HgO = $Hg(CN)_2$ (solid)] + 17·4
$\tfrac{1}{2}$[2HCN (gas) + HgO = $Hg(CN)_2$ (solid) + H_2O (gas)] + 18·3

We will compare this last result with the heat of formation of mercuric chloride.

$\tfrac{1}{2}$[2HCl (gas) + HgO = $HgCl_2$ (solid) + H_2O (gas)] gives off + 23·5,

which value exceeds that of formation of mercuric cyanide by 4·8 only.

These figures, and the conclusions resulting from them, will be referred to again.

2. *Formation of mercuric cyanide from the elements.*

$$\tfrac{1}{2}[Hg\ (liq.) + C_2\ (diamond) + N_2\ (gas) = Hg(CN)_2\ (solid)]$$
absorbs − 25·4 Cal.

Let the initial system be—

$$\tfrac{1}{2}[Hg + C_2 + N_2 + H_2 + O]\ ;$$

and the final system—

$$\tfrac{1}{2}[Hg(CN)_2\ (solid) + H_2O\ (liquid\ and\ separate)]\ ;$$

we pass from one to the other, by the two following steps:—

First Step.

$\tfrac{1}{2}$(Hg + O = HgO) gives off	...	...	+ 15·5
H + C + N = HCN (in solution) absorbs	...	...	− 23·4
Union of these two bodies gives off ...	...	...	+ 15·5
Separation of $Hg(CN)_2$ (solid) gives off	...	...	+ 1·5
	Sum	...	+ 9·1

Second Step.

$\tfrac{1}{2}$[H_2 + O = H_2O (liquid)]	...	...	+ 34·5
$\tfrac{1}{2}$[Hg + C_2 + N_2 = $Hg(CN)_2$ (solid)] ...	...	...	x
	Sum	...	+ 34·5 + x

$$x = -25{\cdot}4.$$

The salt in solution, − 26·9.

There is, therefore, absorption of heat in the formation of mercuric cyanide from the elements; exactly as in the case of hydrocyanic acid. The figures even are very much the same (p. 312).

3. But, on the contrary, the union of gaseous cyanogen with liquid mercury at the ordinary temperature—

$$\tfrac{1}{2}[Hg\ (liquid) + (CN_2)\ (gas) = Hg(CN)_2\ (solid)],\ gives\ off$$
$$+ 37{\cdot}3 - 25{\cdot}4 = + 11{\cdot}9.$$

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This quantity is 19·5 less than the heat disengaged in the direct formation of mercuric chloride—

$$\tfrac{1}{2}[Hg\ (liquid) + Cl_2\ (gas) = HgCl_2\ (solid)] + 31{\cdot}4.$$

4. The same quantity of heat is, on the contrary, absorbed in the ordinary preparation of cyanogen, by the decomposition of mercuric cyanide. To this must be added the heat of vaporisation of the mercury, which brings the absorption of heat to about − 19·4 for the reaction—

$$\tfrac{1}{2}[Hg(CN)_2\ (solid) = Hg\ (gas) + (CN)_2\ (gas)].$$

We may observe that this result is very near that (− 22·4) which accompanies the analogous decomposition of mercuric iodide into gaseous iodine and gaseous mercury. But this last reaction is accompanied by phenomena of dissociation due to the opposite tendency of iodine and mercury to recombine—a tendency which does not exist on the part of the components of mercuric cyanide.[1]

5. *Substitution of chlorine for the cyanogen and formation of cyanogen chloride.* The simple substitution of gaseous chlorine for gaseous cyanogen—

$$\tfrac{1}{2}[Hg(CN)_2\ (solid) + Cl_2\ (gas) = HgCl_2\ (solid) + (CN)_2\ (gas)],$$

assuming the salts to be either in the solid state or in solution (the heats of solution of both salts are the same), would give off + 19·4.

In fact, this substitution is accompanied by a simultaneous formation of cyanogen chloride—

$\tfrac{1}{2}[Hg(CN)_2\ (solid) + 2Cl_2 = HgCl_2\ (solid) + 2CNCl\ (gas)]$ gives off + 21·3,

or, if the cyanogen chloride be supposed liquid, + 29·6.

All the bodies being in solution except the chlorine, we must add to this quantity the heat of solution of cyanogen chloride.

In fact, the heat given off in this reaction, all the bodies except the chlorine being in solution, was measured and found to be = + 27·5 (the cyanogen chloride being also in solution).

This figure seems to indicate that the heat of solution of gaseous cyanogen chloride is very near its heat of liquefaction, as might be expected. Unfortunately, this action is not instantaneous, and this fact diminishes the certainty of accuracy of the estimates, and leads us to fear some complication, attributable to secondary reactions of the chlorine on the water.

6. *Reciprocal displacements of the hydrochloric and hydrocyanic acids.* According to the above remarks, the formation of mercuric cyanide in solution, from the acid in solution and precipitated mercuric oxide, gives off + 15·48, *i.e.* + 6·02 more than that for mercuric chloride (+ 9·46). The same difference

[1] "Annales de Chimie et de Physique," 5e série, tom. xviii. p. 382.

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exists in the solid salts, if we always reckon from the diluted hydracids. These latter being monobasic, the thermal inequality that has been just mentioned indicates that dilute hydrocyanic acid must entirely displace hydrochloric acid from its combination with mercuric oxide.

Here is an experiment that fully bears out this supposition:

$$\left.\begin{matrix}\frac{1}{2}[Hg(CN)_2\ (1\ eq. = 16\ litres) + 2HCl\ (1\ eq. = 4\ litres)] + O \\ \frac{1}{2}[HgCl_2\ (1\ eq. = 16\ litres) + 2HCN\ (1\ eq. = 4\ litres)] + 5{\cdot}9\end{matrix}\right\} \begin{matrix}M - M_1 = +5{\cdot}9 \\ \text{calculated} + 6{\cdot}0\end{matrix}$$

The reaction is all the more remarkable, as, according to thermal observations made, the dilute hydrochloric acid completely displaces the hydrocyanic acid in dissolved potassium cyanide. It was, moreover, easy to foresee that this would be the case in the last instance, for

$$\left.\begin{matrix}\frac{1}{2}[2HCN\ (\text{in solution}) + K_2O\ (\text{diluted})]\ \text{gives off} + 2{\cdot}96 \\ \frac{1}{2}[2HCl\ (\text{in solution}) + K_2O\ (\text{diluted})] \quad ,, \quad ,, + 13{\cdot}59\end{matrix}\right\} M_1 - M = 10{\cdot}63.$$

The decomposition of dissolved mercuric chloride by dilute hydrocyanic acid is all the more remarkable from the fact that solid mercuric cyanide is decomposed by concentrated hydrochloric acid; it is in this way that pure hydrocyanic acid is prepared. But this decomposition—the opposite of that which takes place in weak solutions—is easily explained by thermal theories. In fact, it is due to the action of the anhydrous hydrochloric acid contained in the liquors, when we are operating without heat; or formed under the influence of heat, when we proceed by distillation. Now, this anhydrous hydracid possesses, in relation to the hydrate of the same acid, the energy which the latter has lost in forming a definite hydrate; the magnitude of which energy is sufficient to reverse the reaction.[1]

Moreover, hydrochloric acid gas displaces, immediately and without heat, the hydrocyanic acid gas of crystallised mercuric cyanide. This process for preparing the latter gas has been mentioned. According to calculation, the reaction disengages + 5·2 Cal. Attention[2] has already been called to these two reactions and their mechanism, which is frequently met with under other circumstances, such as when we are comparing the reactions of concentrated acids or alkalis with those of the same acids or alkalis diluted. It is the existence of a certain proportion of acid (or alkali), either not combined with water or combined in the state of a less advanced hydrate in the concentrated liquids, and also the formation of such an acid, dehydrated under the influence of heat, that causes the inverse reaction; and this is in proportion to the excess of energy that the anhydrous acid possesses, in comparison with the hydrate of

[1] "Annales de Chimie et de Physique," 5ᵉ série, tom. iv. p. 465, and 4ᵉ série, tom. xxx. p. 494.

[2] "Essai de Mécanique Chimique," tom. ii. p. 547.

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the same acid, with which it co-exists in the liquors. This excess of energy exactly measures the tendency to produce the inverse reaction, which, however, ceases as soon as the anhydrous hydracid contained in the liquor is saturated.

But, on the contrary, the reaction could not be foreseen, as has been supposed by various writers,[1] from the knowledge of the quantity of heat disengaged in the dilution of the concentrated acid, the bulk of which becomes a dilute acid. Not only is this mode of prediction not justified in principle, since it makes no distinction between the anhydrous acid and its hydrates in solution, but it leads to conclusions which are quite contradicted by experiment. For example, mercuric cyanide is still decomposed in the cold by hydrochloric acid of a density 1·10 (which nearly corresponds to $HCl + 7H_2O$); the dilution of such a hydrochloric solution gives off only 1·7 Cal. Now, this excess would have to be equal to + 6·0 for the reaction to be reversed, according to the theory that we must reject; *i.e.* that the inversion is solely due to the heat of dilution taken in the mass. This excess is so great that the dilution of even the most concentrated hydrochloric acid could not make up for it.

The greater number of reciprocal displacements give rise to the same observations, the heat disengaged by the dilution of concentrated acids or alkalis being scarcely ever sufficient to supply the whole of the body in solution with the energy necessary to reverse the chemical reaction; whereas this energy is, on the contrary, supplied by the hydration of the portion of acid (or alkali) which existed in the liquor in a dissociated state.

7. But to return to mercuric cyanide. Theory indicates that the displacement of hydrochloric acid by hydrocyanic acid in mercuric chloride may be observed still more clearly if we substitute an alkaline cyanide for the free hydrocyanic acid. In fact, in this case, we shall get, besides, the difference of the heats of neutralisation of both acids by the alkali. This is confirmed by experiment.

$\frac{1}{2}$[2KCN (1 equiv. = 8 litres) + $HgCl_2$ (1 equiv. = 4 litres)] disengages + 16·7.

$\frac{1}{2}$[2KCl (1 equiv. = 8 litres) + $Hg(CN)_2$ (1 equiv. = 4 litres)] disengages + 0.

Now, calculation gives—

$$(M - M_1) - (M' - M'_1) = (13·6 - 3) - (9·5 - 15·5) = + 16·6,$$

a result quite consistent with the above. Thus, the reality of a double integral interchange between the bases and acids in solution is fully established. This is one of the most glaring cases in which the so-called saline thermo-neutrality which was

[1] "Annales de Chimie et de Physique," 5e série, tom. iv. p. 464.

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formerly accepted is found to be at fault. The result observed agrees perfectly with that calculated, when this calculation is based upon the hypothesis of a total conversion into mercuric cyanide and potassium chloride in solution. Moreover, this does not affect the reciprocal reaction between the two last salts when in solution; *i.e.* the formation of a double cyanide, which will be discussed presently.

8. A reciprocal action of this kind is easily shown between potassium cyanide in solution, and solid mercuric iodide, which enters into solution—

$\frac{1}{2}$[HgI_2 (solid) + 4KCN (1 equiv. = 16 litres)], total solution, + 9·7.

The solution of the solid body takes place, in this case, with a considerable disengagement of heat, on account of the heats of formation of the double salts that are generated and remain in solution.

9. The formation of the mercuric oxycyanides from the combination of the cyanide with the oxide may be mentioned here. This combination is effected with disengagement of heat (Joannis)—

$\frac{1}{2}$[$Hg(CN)_2$ (solid) + HgO = $Hg(CN)_2$,HgO (solid)] gives off + 1·2.

This oxycyanide, when heated, explodes, in consequence of the combustion of part of its carbon by the oxygen which it contains.

§ 8. Silver Cyanide.

1. *Formation from the acid and base.*

Some experiments were made on the heat of formation of silver cyanide.

(*a*) $AgNO_3$ (1 equiv. = 16 litres) + HCN (1 equiv. = 4 litres) + 15·72,

from which is got—

$\frac{1}{2}$[2HCN (in solution) + Ag_2O (precipitated) = 2AgCN (precipitated)] gives off + 20·9.

(*b*) $AgNO_3$ (1 equiv. = 16 litres) + KCN (1 equiv. = 4 litres) + 26·57,

from which is got—

$\frac{1}{2}$[HCN (in solution) + Ag_2O (precipitated) = 2AgCN (precipitated)] gives off + 20·9,

a value identical with the above. It is, moreover, almost the same as the heat disengaged in the formation of silver chloride.

Again, we get from the above results:

$\frac{1}{2}$[2HCN (liquid) + Ag_2O (precipitated) = 2AgCN + H_2O (liquid)] + 21·3
$\frac{1}{2}$[2HCN (gas) + Ag_2O (precipitated) = 2AgCN + H_2O (liquid)] + 27·0
$\frac{1}{2}$[2HCN (gas) + Ag_2O (precipitated) = 2AgCN + H_2O (gas)]... + 22·2

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this last value being only approximate, on account of the physical changes experienced by the silver oxide and cyanide. It is less by a third than the heat, 33·2, given off in the analogous formation of silver chloride. These values explain why hydrocyanic acid displaces nitric acid from its combination with silver oxide, and why silver cyanide resists the action of dilute nitric acid.

2. Formation from the elements.

1. $Ag + C$ (diamond) $+ N + AgCN$ absorbs $- 13{\cdot}6$.

The calculation of this value is as follows:—
Initial system:

$$\tfrac{1}{2}[Ag_2 + C_2 + N_2 + H_2 + O],$$

Final system:

$$\tfrac{1}{2}[2AgCN \text{ (solid)} + H_2O \text{ (liquid)}].$$

First Step.

$\frac{1}{2}[Ag_2 + O = Ag_2O]$ disengages	$+ 3{\cdot}5$
$H + C + N = HCN$ (diluted) absorbs	$- 23{\cdot}4$
$\frac{1}{2}[Ag_2O + 2HCN$ (diluted)] disengages	$+ 20{\cdot}9$
Sum ...	$+ 0{\cdot}8$

Second Step.

$Ag + C + N = AgCN$	x
$\frac{1}{2}[H_2 + O = H_2O]$	$+ 34{\cdot}5$
Sum ...	$+ 34{\cdot}5 + x$

whence, $x = - 33{\cdot}7$.

2. Again, we have—

$$Ag + CN \text{ (gas)} = AgCN \text{ gives off } + 3{\cdot}6.$$

Let us compare the differences observed between the heats of formation of the chloride and cyanide, formed by the same metal or system of elements. For potassium, the difference is—

$$105 - 67{\cdot}6 = + 37{\cdot}4;$$

for ammonium—

$$76{\cdot}7 - 40{\cdot}5 = + 36{\cdot}2.$$

The value here is almost the same. But the figures become very unequal for metallic salts, such as those from silver:

$Ag + Cl$ gives off	$+ 29{\cdot}2$	difference $= + 25{\cdot}6$
$Ag + CN$ gives off	$+ 3{\cdot}6$	
$\frac{1}{2}[Hg + Cl_2]$ gives off	$+ 31{\cdot}4$	difference $= + 19{\cdot}5$
$\frac{1}{2}[Hg + CN_2]$ gives off	$+ 11{\cdot}9$	

For silver and mercury we observe that the value is only half that relating to alkaline salts.

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The same differences exist for cyanides when compared with bromides (Br gas)—

						Difference.
[K]	...	...	...	...	85·4 − 67·6 =	17·8
[Hg]	...	...	...	...	22·4 − 11·9 =	10·5
[Ag]	...	...	...	...	19·7 − 3·6 =	16·1

Also between cyanide and iodides (I gas)—

						Difference.
[K]	...	...	...	...	100·4 + 67·5 =	32·8
[Hg]	...	...	...	...	30·4 + 11·9 =	18·1
[Ag]	...	...	...	..	27·7 + 3·6 =	24·1

These inequalities result from the great quantity of heat disengaged by the union of the hydrocyanic acid with metallic oxides as compared with the small quantity disengaged in the union of the same acid with alkalis.

§ 9. Double Cyanides.

It is now necessary to find the heat of formation of double cyanides, such as the cyanides of mercury and potassium, silver and potassium, and also that of ferrocyanides, which are worthy of particular attention.

1. *Cyanide of mercury and potassium:* $Hg(CN_2), 2KCN$. This compound offers a remarkable example of a double salt which exists and is even undoubtedly generated in solutions. In fact, it was found that its two components, when in solution, give off a great quantity of heat if merely mixed together—

$$\tfrac{1}{2}[Hg(CN)_2 \text{ (1 equiv. = 16 litres)} + 2KCN \text{ (1 equiv. = 4 litres)}] + 5{\cdot}8.$$

This quantity represents nearly two-thirds of the heat disengaged by the union of the two salts when in the solid state. The latter value is calculated by means of the following data:—

KCN, on being dissolved in 40 times its weight of water	− 2·96
$\frac{1}{2}[Hg(CN)_2]$, on being dissolved in 40 times its weight of water ...	− 1·50
$\frac{1}{2}[2KCN, Hg(CN)_2]$, on being dissolved in 40 times its weight of water	− 6·96

These data go to show that the combination

$$\tfrac{1}{2}[Hg(CN)_2 \text{ (dry)} + 2KCN \text{ (dry)} = Hy(CN)_2, 2KCN \text{ (dry)}], \text{ disengages } + 8{\cdot}3,$$

which is a considerable quantity of heat. It approaches, and even exceeds, the heat disengaged in the formation of many metallic salts, from the anhydrous acid and base. However, the double cyanide, in solution, is immediately decomposed by diluted hydrochloric acid, with separation of its components; the mercuric cyanide being regenerated unaltered in the liquor, and the potassium cyanide being converted into potassium chloride.

This was discovered by measuring the heat disengaged in the

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reaction. This measurement proves, in fact, that dilute hydrochloric acid, acting on the solution of the double cyanide, separates the components, with reproduction of potassium chloride and hydrocyanic acid:

$[\frac{1}{2}Hg(CN)_2$, 2KCN (20 litres) + 2HCl (1 equiv. = 2 litres], + 5·2
" " " − 4HCl " + 0

The calculation, based upon these last data, indicates the following value: + 3·0 + 5·8 + 5·2 = + 14·0 for the heat disengaged in the union of hydrochloric acid with potash; a value which agrees to all intents with the actual value + 13·6, that is, if the liquors are as much diluted as in the above.

2. *Cyanide of silver and potassium:* AgCN, KCN. This salt, so much used in electro-plating, acts in a manner similar to the above. It is formed by the direct action of potassium cyanide in solution on precipitated silver cyanide, the latter becoming dissolved with disengagement of heat—

KCN (1 eq. = 4 litres) + AgCN (precipitated) + water (20 litres) gives off + 5·6.

The reaction disengages almost the same quantity of heat as that in the case of mercuric cyanide, notwithstanding the solid state of the silver cyanide.

This is a fresh instance of the solution of a precipitate being effected with disengagement of heat, in consequence of the formation of a double salt. The phenomena are dependent on this formation, independently of the solubility or insolubility of the original metallic cyanide (mercuric or silver), as the double salt is formed with disengagement of heat, and is stable in the presence of excess of the dissolving agent.

It was also found that the solution of the soluble salt—

AgCN, KCN (solid) (1 part = 40 parts of water), absorbs − 8·55.

We conclude from these data, and also the heat of solution of potassium cyanide, that the combination—

AgCN (precipitated) + KCN (dry) = AgCN, KCN (dry), disengages + 11·2.

The double salt in solution is immediately decomposed by dilute hydrochloric acid, with reproduction of potassium chloride and hydrocyanic acid, as is proved by thermal measurements. At the same time a precipitate of silver chloride is produced, mixed with a considerable proportion of cyanide, as might be expected; for the formation of both salts from the diluted hydracids and precipitated silver oxide causes the liberation of about the same quantity of heat (+ 20·9).

The double cyanide of silver and potassium, however, constitutes a firmer combination than is usually met with in ordinary double salts. In fact, dilute acetic acid separates silver cyanide from it only in a very incomplete manner, giving

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off only + 1·7 Cal., instead of + 4·8, which would correspond to a total decomposition. Tartaric acid gives similar results. It would seem, then, that the liquors contain a hydro-argento-cyanic acid, already mentioned by Meillet; a complex acid, which can only exist in the presence of water and another acid, so as not to give rise to phenomena of equilibrium, and consequently to a partial decomposition. The solutions of this complex acid produce results in silver-plating that are almost as well marked as those produced by alkaline cyanide solutions, as there was occasion to prove.

This compound forms a very remarkable intermediate step in the formation of those special molecular types that constitute the complex cyanides.

3. *Potassium ferrocyanide.* A more decided stability characterises the double cyanide of potassium and iron, known as ferrocyanide. Although the thermal study of its formation presents great difficulties, owing to the fact that we cannot start with isolated iron cyanides, nevertheless it is undoubtedly worth while giving the results of the experiments performed, with the admission that they are, no doubt, imperfect.

4. *The heat of solution* of both dry and hydrated potassium ferrocyanide was first measured, the former in fifty parts of water, the latter in forty parts of water. It was found that at 11°

$\frac{1}{2}[K_4Fe(CN)_6, 3H_2O]$ (211·2 grms.), in dissolving, absorbs − 8·46.
$\frac{1}{2}[K_4Fe(CN)_6$ (dry)] „ „ − 5·98.

From these figures it follows that the union of the water with the dry salt—

$\frac{1}{2}[K_4Fe(CN)_6 + 3H_2O$ (solid) $= K_4Fe(CN)_6, 3H_2O$ (crystal)], gives off + 0·34, or + 0·11 for each $\frac{1}{2}(H_2O)$,

a quantity which is very small, but, according to certain experiments,[1] comparable to that which is disengaged in the formation of the hydrated calcium and copper acetates.

5. *The heat of neutralisation* of hydroferrocyanic acid by bases cannot be conveniently measured directly, on account of the difficulty of obtaining the free acid in a perfect state of purity. The latter object was attempted by indirect means, *i.e.* by displacing the acid from its salts by more powerful acids.

On mixing a diluted solution of ferrocyanide—

$$\frac{1}{2}[K_4Fe(CN)_6] = 4 \text{ litres},$$

with diluted hydrochloric acid (1 eq. = 2 litres), we observe that there is absolutely no change of temperature, either because there is no reaction, or because the two acids disengage the same quantity of heat in acting on the potash, in which case

[1] "Annales de Chimie et de Physique," 5ᵉ série, tom. iv. p. 127.

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they would share between them the base in the liquor. This last supposition seems the more probable.

In fact, on mixing the ferrocyanide with dilute sulphuric acid we actually observe a progressive division of the base between the acids and a displacement, which tends to become total in the presence of a great excess of sulphuric acid. Among the various experiments that were made with regard to this question, the following only will be quoted:—

$\frac{1}{2}[K_4Fe(CN)_6$ (6 litres) + H_2SO_4 (1 eq. = 2 litres)] disengages + 1·107.

$\frac{1}{2}[K_4Fe(CN)_6$ (6 litres) + $2eH_2SO_4$ (1 eq. = 2 litres)] disengages + 0·181.

Upon continuing the progressive additions of sulphuric acid, an absorption of heat is produced owing to the formation of the bisulphate.

With a large excess, added all at once—

$\frac{1}{2}[K_4Fe(CN)_6$ (4 litres) + $10H_2SO_4$ (1 eq. = 2 litres)] + 0·966.

These phenomena may be compared to those in the reaction of sulphuric acid upon chlorides,[1] although the values are somewhat different. They also show a progressive division of the base between the two acids. If we admit that $\frac{1}{2}[10H_2SO_4]$ are sufficient to abstract almost the whole of the potash from the ferrocyanide, according to what happens in the case of chlorides, nitrates, etc., we can calculate the heat, X, disengaged in the action of dissolved hydroferrocyanic acid on diluted potash. In short, + 15·7 being the heat disengaged by the action of sulphuric acid on potash, and − 1·75 the heat absorbed in the action of $\frac{1}{2}[4H_2SO_4$ (diluted)] on $\frac{1}{2}[K_2SO_4]$ in solution (so as to form bisulphate), we shall get for the reaction we are seeking—

$\frac{1}{2}[\frac{1}{2}(H_4Fe(CN)_6$ = 4 litres) + K_2O (1 eq. = 2 litres)] gives off $X = 15·71 - 1·75 - \frac{1}{2}(0·97) = + 13·5$.

This number is, to all intents, the same as that which represents the heat disengaged (13·6) by the combination of hydrochloric and nitric acids with potash, whence it follows that hydroferrocyanic acid is a powerful one, and may be compared with the mineral acids. We know, in fact, that it displaces carbonic and acetic acids. The apparent absence of thermic reaction between hydrochloric acid and ferrocyanide in solution is consistent with these results.

6. Nothing is easier than to pass from this to the formation of *Prussian blue*. It was found, in fact, that $\frac{1}{12}[3K_4Fe(CN)_6$ = (4 litres) + $2Fe_2(SO_4)_3$ (1 equiv. = 2 litres) = $(Fe_7(CN)_{18}$ (precip.) + $6K_2SO_4$ (diss.)] disengages + 2·54 to + 2·78, the

[1] "Annales de Chimie et de Physique," 4e série, tom. xxx. p. 524.

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heat disengaged gradually increasing with the time; as frequently happens in the formation of amorphous precipitates.[1] Similarly:

$\frac{1}{12}[3(K_4Fe(CN)_6 = 4 \text{ litres}) + 2Fe_2(NO_3)_6 (1 \text{ equiv.} = 2 \text{ litres}) = Fe_7(CN)_{18})$ (precipitated) $+ 2KNO_3$ (in solution)] disengages $+ 0{\cdot}725$.

According to the result furnished by the ferric sulphate, the substitution of potash for ferric oxide (K_2O for Fe_2O_3) in Prussian blue gives off $+ 7{\cdot}2$; and according to the result furnished by the nitrate, $+ 7{\cdot}2$; thus the two results agree. Admitting that in the formation of potassium ferrocyanide,

$\frac{1}{2}[H_4Fe(CN)_6$ (diluted) $+ 2K_2O$ (diluted)], disengages $+ 13{\cdot}5 \times 2 = + 27$,

we conclude that the formation of Prussian blue, with the same acid and precipitated ferric oxide—

$\frac{1}{6}[3H_4Fe(CN)_6$ (diluted) $+ 2Fe_2O_3$ (precipitated)], gives off $+ 6{\cdot}3 \times 2 = + 12{\cdot}6$.

The value $6{\cdot}3$ is little different from the value $5{\cdot}7$, which represents the heat of combination of nitric and hydrochloric acids with ferric oxide; this is a fresh proof of the analogy existing between hydroferrocyanic acid and the mineral acids. However $+ 6{\cdot}3$ is greater than $5{\cdot}7$, which explains why diluted hydrochloric acid does not decompose Prussian blue, with formation of ferric chloride.

7. Hydrocyanic acid, one of the weakest acids known, thus constitutes, when combined with ferrous cyanide, a powerful acid, comparable in every respect with nitric, acetic, and hydrochloric acids. This is a fresh proof, which helps to establish the theory that the acid properties that are most marked, even in compounds containing carbon and hydrogen, are not necessarily connected in any way with the presence or proportion of oxygen.

8. We now have to measure the heat disengaged in the formation of ferrocyanide. The following results were found:—

$\frac{1}{2}[FeSO_4$ (1 equiv. = 2 litres) $+ 2Fe_2(SO_4)_3$ (1 equiv. = 2 litres) $+ 6K_2O$ (1 equiv. = 2 litres)] gives off $+ 23{\cdot}2$.

Adding to the above mixture $\frac{1}{2}[6HCN$ (1 equiv. = 4 litres)], we observe a fresh disengagement of $+ 39{\cdot}3$, which represents the formation of ferrocyanide from hydrocyanic acid and the two oxides—

$\frac{1}{2}[6HCN$ (in solution) $+ 2K_2O$ (in solution) $+ FeO$ (precipitated) $= K_4Fe(CN)_6$ (in solution)] gives off $+ 39{\cdot}3$.

[1] "Annales de Chimie et de Physique," 5e série, tom. iv. pp. 174, 181.

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As a proof,

$$\tfrac{1}{2}[6HCl] \text{ (1 equiv. = 2 litres)}$$

was added to the liquid; this gave off + 25·0 Cal., with the production of an abundant precipitate of Prussian blue; the heat disengaged varied, during this precipitation, from 23 to 25. To sum up, the hydrochloric acid should produce the following reactions:—

$$\left.\begin{array}{l}\tfrac{1}{2}[2HCl \text{ (diluted)} + K_2O \text{ (diluted)} = 2KCl \text{ (diluted)}] \ \ldots \quad + 13{\cdot}6 \\ \tfrac{1}{2}[6HCl \text{ (diluted)} + Fe_2O_3 \text{ (precipitated)} = Fe_2Cl_6 \text{ (diluted)}] \quad + 11{\cdot}4 \\ \tfrac{1}{6}[2Fe_2Cl_6 \text{ (diluted)} + 3K_4Fe(CN)_6 \text{ (in solution)} = Fe_7(CN)_{18} \\ \quad + 12KCl \text{ (diluted)}] \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad + 1{\cdot}4\end{array}\right\} + 26{\cdot}4$$

The approximate consistence between the values 25 and 26·4 is as close as can be hoped for in the study of such precipitates, the state of which varies with the conditions.

9. We may conclude, further—

$\tfrac{1}{6}[18HCN \text{ (diluted)} + 3FeO \text{ (precipitated)} + 2Fe_2O_3 \text{ (precipitated)} = Fe_7(CN)_{18} \text{ (precipitated)}]$ gives off + 24·9.

$\tfrac{1}{2}[6HCN \text{ (diluted)} + FeO \text{ (precipitated)} = H_4Fe(CN)_6 \text{ (in solution)}]$, + 12·3.

These values were verified by means of the direct formation of Prussian blue from potassium cyanide and the two sulphates of iron:

$\tfrac{1}{6}[18KCN \text{ (1 equiv. = 2 litres)} + 3FeSO_4 \text{ (1 equiv. = 2 litres)} + 2Fe_2(SO_4)_3 \text{ (1 equiv. = 2 litres)} = Fe_7(CN)_{18} \text{ (precipitated)} + 9K_2SO_4 \text{ (diluted)}]$ gives off + 37·5.

The difference between the heat of formation of the alkaline sulphate and that of the iron sulphates, reckoning from the oxides, being 12·5 + 11·1 − 47·1 = − 23·2, and the heat of formation of 3KCN from potash being 8·9, we can easily determine from these data the heat disengaged in the formation of Prussian blue from hydrocyanic acid:

$\tfrac{1}{6}[18HCN \text{ (diluted)} + 3FeO + 2Fe_2O_3 = Fe_7(CN)_{18}]$ gives off 37·5 + 8·9 − 23·2 = + 23·2;

a value sufficiently near to 24·9, which was obtained in another way, but is a less accurate result.

10. It is now possible to draw a few general conclusions from these results.

The first that occurs to us relates to the heat disengaged in the formation of the ferrocyanide, starting from hydrocyanic acid or from potassium cyanide.

$\tfrac{1}{2}[6HCN \text{ (in solution)} + 3K_2O \text{ (diluted)}]$ gives off + 8·7.

$\tfrac{1}{2}[6HCN \text{ (in solution)} + 2K_2O \text{ (diluted)} + FeO \text{ (precipitated)}]$ gives off + 39·3.

We see that the substitution of ferrous oxide for potash, with

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formation of ferrocyanide, gives off a considerable proportion of heat: viz. 39·3 − 8·7 = + 30·6. Moreover, only a single equivalent of ferrous oxide is required to constitute hydroferrocyanic acid.

These figures also explain the displacement observed, and correspond to the constitution of a new molecular type,—that of hydroferrocyanic acid.

In fact, we conclude from them that

$\frac{1}{2}$[6HCN (in solution) + FeO (precipitated)] gives off + 12·3,

which quantity exceeds the heat (+ 9·0) disengaged by the combination of $\frac{1}{2}$[$3K_2O$ (diluted)] with $\frac{1}{2}$[6HCN].

There are here two simultaneous reactions, viz. the union of six molecules of hydrocyanic acid into a type six times as condensed, and the reaction of the ferrous oxide which enters into the constitution of this new type: $H_4Fe(CN)_6$.

In the same way, for Prussian blue, the fact has been established elsewhere that

$\frac{1}{6}$[$3H_4Fe(CN)_6$ (diluted) + $2Fe_2O_3$ (precipitated)] gives off + 12·6 = 6·3 × 2,

or almost the same quantity as in the union of the same oxide with diluted hydrochloric and nitric acids.

From hydrocyanic acid itself we get—

$\frac{1}{6}$[18HCN (diluted) + 3FeO + $2Fe_2O_3$ = $Fe_7(CN)_{18}$ (precipitated)] + 24·9 = 8·3 × 3.

The magnitude of this last quantity, which is three times that of the heat disengaged by potash in its combination with hydrocyanic acid, enables us, as before, to account for the formation of the new molecular type of ferrocyanides, and, in a more general manner, for the formation of double cyanides.

11. This consistency in effects also explains, by the greater quantity of heat disengaged, the greater apparent affinity presented by ferrous oxide, as compared with potash, in its union with hydrocyanic acid; this is contrary to what happens in the comparison of the formation of the ordinary oxysalts, sulphates, nitrates, acetates, etc., from diluted acids and alkaline bases, with that of those salts from the same salts with metallic oxides.

12. Could we not explain by some similar circumstance why silver and mercuric oxides, as well as ferrous oxide, give off more heat than diluted potash in their combination with hydrocyanic acid? In a word, are mercuric and silver cyanides really represented by the simple formulæ

$$AgCN \text{ and } Hg(CN)_2,$$

those of potassium cyanide and hydrocyanic acid being KCN and HCN? or ought we rather not regard them as being them-

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selves cyanides of a more condensed type, such as $Hg_2(CN)_4$ and $Ag_2(CN)_2$? The heat disengaged by their union with potassium cyanide, so as to form double cyanides, such as $K_2Hg(CN)_4$; $KAg(CN)_2$, even in dilute solutions, would support this opinion; as it would result from the transition from the simple type potassium cyanide to the complex type constituting the double cyanides—

$$Hg(CN)_2 + 2KCN = HgK_2(CN)_4$$
$$AgCN + KCN = AgK(CN)_2.$$

Besides, hydrocyanic acid is not the only acid that gives rise to the general inversion of ordinary affinities, as shown by the corresponding thermal effects, between the alkaline oxides and metallic oxides. It is exactly the same with hydrosulphuric acid.[1]

13. However it may be with regard to these last considerations, it remains no less a fact that metallic oxides give off more heat than alkaline bases in uniting with hydrocyanic acid; which explains why they displace them. It may be repeated that thermo-chemistry thus explains the constitution of complex cyanides—new molecular types, very superior to the primitive type, as regards the energy of their affinities towards bases, and the stability of the resultant salts, very superior to hydrocyanic acid, which aids in their formation by its condensation.

Hydrocyanic acid, the common generator of these condensed types, is moreover distinguished by the fact that it is formed from the elements with an absorption of heat amounting to 29·5; in other words, its formation has stored up an excess of energy that gives it a special tendency towards successive combinations and molecular condensations.

14. We will give, in conclusion, the heat of formation of potassium ferrocyanide from its elements, a quantity that enters into the study of certain explosive substances.

From cyanogen, we should get—

$$\tfrac{1}{2}[2K_2 + Fe + 3(CN)_2 = K_4Fe(CN)_6 \text{ (solid)}] \text{ gives off } + 183{\cdot}6,$$
$$\text{or } + 61{\cdot}2 \times 3.$$

From the elements—

$$\tfrac{1}{2}[2K_2 + Fe + 6C + 3N_2 = K_4Fe(CN)_6] + 71{\cdot}7, \text{ or } + 23{\cdot}9 \times 3.$$

These values are near those that correspond to the formation of potassium cyanide; viz. from cyanogen, + 67·6; and from the elements, + 30·3.

The hydrated salt contains, in addition, three equivalents of water, $3H_2O$, the union of which in a liquid form with the anhydrous salt gave off 2[+ 2·48]; which makes altogether for the crystallised yellow prussiate from the elements and water, + 94·2 Cal.]

[1] See "Annales de Chimie et de Physique," 5e série, tom. iv. p. 186.

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§ 10. Cyanogen Chloride.

1. Cyanogen chloride was prepared in the form of a colourless, dry and pure liquid; its purity was proved by the determination of the chlorine contained in a given weight of the compound. This done, several samples of it were weighed into sealed phials; the weight of these samples was approximately 2 grms.; being 1·946 grm., 2·4675 grms., 2·137 grms., and so on.

2. This cyanogen chloride was converted into carbonic acid (in solution) and ammonium chloride—

$$CNCl \text{ (liquid)} + 2H_2O + \text{water} = CO_2 \text{ (in solution)} + NH_4Cl \text{ (in solution)}.$$

The heat disengaged during this transformation was measured by the following method, which consists in treating the cyanogen chloride with potash and hydrochloric acid successively.

Preliminary operations.—A solution of potash containing about 1 equiv. (47·1 grms.) in 10 litres of liquid was introduced into the calorimeter, a proportion of it being taken that would represent rather more than 3 equiv. for 1 equiv. of chloride (CNCl = 61·5 grms.); *i.e.* about 1 litre of the alkaline solution.

The rate of cooling during an interval of ten minutes, measured before the actual experiment, was found to be *nil;* which is explained by the fact that the temperature of the liquid was 21·51°, that of the enclosing vessel being 21·31°.

The phial containing the cyanogen chloride is surrounded with a thick platinum wire, wound into a spiral, so as to add weight to the phial and form a system that will remain at the bottom of the water whether the phial be full, empty, or giving off gases. This system is placed in a dry glass tube, which is surrounded with ice, a little thermometer and a piece of potash being put by the side of the phial; then we wait until the thermometer records a temperature as near zero as possible; 0·5° for example. It is necessary to take the precaution of cooling the phial beforehand, if we wish to be able to open it afterwards without loss or projection, after its introduction into the calorimeter, seeing that cyanogen chloride boils at 12°, and that it would be violently expelled if the point of the closed phial were broken, in which it had been kept a liquid at a temperature of 21°, in virtue of its own pressure.

First stage of the experiment.—The phial having been thus prepared beforehand, and kept in a cold dry tube (dry, in order to prevent the condensation of moisture on the surface of the phial), the calorimeter is made ready. We then take the platinum spiral surrounding the phial, and plunge the whole,

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spiral and phial, into the calorimeter, the water in which should completely cover the two points of the phial. We, however, keep the lower point from touching the bottom of the calorimeter, so as to prevent the possibility of its getting broken in the course of the subsequent operations. When these preparations are completed, we break the upper point of the phial, by a sharp blow with a platinum hammer against a piece of glass resting on this point, or in some similar way; but the lower point must be carefully kept intact. Under these conditions, cyanogen chloride is at once given off, escaping in gaseous bubbles from the broken point; these are absorbed, as they appear, by the alkaline solution. The operation proceeds with extreme regularity, if all the prescribed precautions have been observed.

Nevertheless, we follow at each minute the course of the calorimetric thermometer. At the end of about 20 minutes, the vaporisation is complete and the maximum temperature attained. It exceeds the original temperature by about 2°. The phial is then completely broken up with the hammer, in order to destroy the last traces of cyanogen chloride, and complete the mixture.

The first stage of the operation converts the cyanogen chloride into potassium chloride and cyanate (or rather isocyanate), mixed with a certain quantity of potassium and ammonium carbonates.

The proportion of these products of a further reaction varies according to the concentration of the potash and various other circumstances; it seems to increase little by little, by a slow reaction. We cannot, therefore, stop at this point, as it does not furnish a reliable basis for calorimetric computations.

Second stage of the experiment.—This is why, when the maximum has been reached and the phial broken, we introduce into the calorimeter a certain quantity of dilute hydrochloric acid, rather more than would be required to exactly neutralise the potash used in the experiment. The temperature of this acid is, moreover, obtained with exactness by special measurement. A new reaction is immediately developed; a reaction which rather rapidly, but not instantaneously, converts the potassium cyanate (iso-) into potassium chloride and carbonic acid in solution. In order to avoid the liberation of this last gas, in consequence of the liquid being mixed with air, this liquid is agitated by means of a stirrer that moves horizontally (p. 147).

The maximum is attained in six minutes. It exceeds the original temperature by about 3°. It lasts three minutes, and then the temperature begins to fall. The progress of this cooling is followed during thirty minutes. The actual experiment lasts about as long.

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During all this time the temperature of the enclosing vessel only varied from 21·21° to 21·37°.

Study of the cooling.—We then take a diluted solution of potassium chloride, occupying the same volume as the above liquid; this is introduced into the same vessel and the temperature raised so as to exceed by 3° that of the enclosing vessel, just given. The progress of the cooling is again followed for ten minutes; then the excess of temperature is reduced to 2° by substituting a suitable volume of a cold solution of the same composition for the heated solution contained in the calorimeter. We then repeat the experiments on the rate of cooling, corresponding to this last excess.[1]

Calculations.—We thus possess all the necessary data for calculating the heat disengaged during the experiment.[2] This calculation is made without the aid of hypotheses, and according to the rules already laid down for hydrocyanic acid (p. 306).

In this way we obtain the quantities of heat disengaged during the two stages of the experiment; or, $q_1 + q_2$. The correction due to the cooling is 8 per cent. for the first stage of the experiment in question; it reaches 12 per cent. for the second stage. The total quantity of heat disengaged represents the conversion of the liquid cyanogen chloride into carbonic acid in solution and ammonium chloride, plus the heat produced in the complete saturation of the potash employed by dilute hydrochloric acid. P being the weight of this potash, it would give off, if treated separately with hydrochloric acid, $\frac{P}{47·1} + 13·6$ Cal. Let q_3 be the quantity of heat disengaged by the conversion of the cyanogen chloride into carbonic acid and ammonium chloride under the influence of pure water; we then get—

$$q_3 = q_1 + q_2 - \frac{P}{47·1}\,13·6 \text{ Cal.}$$

We have now only to multiply the quantity, q_3, by the inverse ratio of the weight, p, employed to the equivalent of cyanogen chloride (61·5 grms.). It was found that $q_3 \times \frac{61·5}{p} = 61·68$ Cal. (according to the average of the experiments). This value represents the heat disengaged in the following reaction:—

$$CNCl \text{ (liquid)} + 2H_2O + \text{water} = CO_2 \text{ (in solution)} + NH_4Cl \text{ (in solution)}.$$

[1] For this method, see "Annales de Chimie et de Physique," 4e série, tom. xxix. p. 158.

[2] The only unknown quantity is the specific heat of liquid cyanogen chloride. The approximate value, 0·4, was taken: it is near enough, on account of the extreme smallness of the corresponding correction.

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3. *Heat of formation of cyanogen chloride from the elements.* This quantity is easily deduced from the above value. Let the initial system be—

$$C + N + Cl + 2H_2 + O_2 + \text{water};$$

and the final system—

$$CO_2 \text{ (gas)} + NH_4Cl \text{ (in solution)}.$$

We pass from one to the other, by two different methods:

FIRST METHOD.

C (diamond) $+ O_2 = CO_2$ (gas)	+ 94·0
Solution of CO_2	+ 5·6
HCl = HCl (in solution)	+ 39·3
$NH_3 = NH_3$ (in solution)	+ 21·0
Union of $NH_3 + HCl = NH_4Cl$ (in solution) ...	+ 12·45
Sum	+ 172·35

SECOND METHOD.

$2(H_2 + O) = 2H_2O$	+ 138
$C + N + Cl = CNCl$ (liquid)	x
$CNCl$ (liquid) $+ 2H_2O$ + water = CO_2 (in solution) + NH_4Cl (in solution)	+ 61·7
Sum	x + 199·7

whence,

$$x = -27{\cdot}35.$$

This is the quantity of heat absorbed during the *formation of cyanogen chloride from the elements*—

C (diamond) + N + Cl = CNCl (liquid) absorbed − 27·35.

We will pass on to the gaseous compound.

4. *Vaporisation of cyanogen chloride.* The heat absorbed in this operation was measured in a direct manner, *i.e.* by submerging in the water of a calorimeter (500 cc.) which was at 20° a phial containing a known weight, 2·069 grms. for instance, of liquid cyanogen chloride. The phial had been cooled beforehand to nearly zero and weighted with a platinum wire, as already described. Only the upper point, instead of being opened directly into the liquid of the calorimeter, was fitted with a little worm through which the gaseous chloride was given off. This gas was then conveyed outside the calorimeter, and absorbed by a solution of potash. The operation lasts about twenty-five minutes. All calculations being made, the following number was found for the vaporisation of CNCl (= 61·5 grms.); − 8·76 Cal. absorbed.

This value comprises—

(*a*) The heat of vaporisation of cyanogen chloride at + 12·7°.

(*b*) The heat absorbed by the liquid, which has been raised from 1° to + 12·7°.

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(*c*) The heat absorbed by the gas, which has been raised from 12·7° to 19·7° (the average temperature during the vaporisation).

These two last quantities are relatively small. They could only be estimated exactly if we knew the specific heats of cyanogen chloride in the liquid and the gaseous states at the temperatures indicated. In default of any direct data, approximate values were used; the total value of these two quantities, moreover, representing a very small quantity as compared with the heat of vaporisation itself. Let us admit for these specific heats the mean value + 0·4, deduced from observation made on similar liquids. Consequently, the heat absorbed in the accessory operations (*b* and *c*) will be estimated at 0·46; a correction entailing probable error amounting to not more than a fourth of its value. The heat of vaporisation of cyanogen chloride will be, for CNCl (= 61·5 grms.), − 8·3 Cal.

Thus the formation of gaseous cyanogen chloride from its elements—

$$C\ (\text{diamond}) + N + Cl + CNCl\ (\text{gas}),\ \text{absorbs} - 35{\cdot}7.$$

These figures exceed in absolute value the heat absorbed in the formation of hydrocyanic acid; for—

$$H + C + N = HCN\ (\text{gas}),\ \text{absorbs} - 29{\cdot}5.$$

The formation of cyanogen chloride from the elements is, therefore, endothermal, like that of hydrocyanic acid, but even in a higher degree. This circumstance explains why cyanogen chloride is so apt to undergo polymeric transformations and other condensations.

5. *Union of cyanogen with chlorine.* From the above data we deduce—

$$CN\ (\text{gas}) + Cl\ (\text{gas}) = CNCl\ (\text{gas})\ \text{gives off} + 37{\cdot}3 - 35{\cdot}7 = + 1{\cdot}6.$$

$$CN + Cl = CNCl\ (\text{liquid}) + 9{\cdot}9.$$

These values were checked by another method.

We know that cyanogen chloride is easily formed by the action of mercuric cyanide, in solution, on chlorine. The heat disengaged in this operation was measured.

$$\tfrac{1}{2}[Hg(CN)_2\ (\text{in solution}) + 2Cl_2\ (\text{gas}) = HgCl_2\ (\text{in solution}) + 2CNCl\ (\text{in solution}).$$

The value + 17·5 Cal. was found.

The calculation, supposing the cyanogen chloride to be liquefied instead of being in solution, would give + 29·6; the difference does not exceed the limits allowed in experiments of this kind, or the differences which exist between solution and liquefaction. This is, therefore, at least an approximate check on the heat of formation of cyanogen chloride.

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The heat of formation of liquid cyanogen chloride from chlorine and cyanogen, or + 9·9, is quite comparable to the heat of formation of iodine chloride and iodine bromide, under the same form—

$$I\ (gas) + Cl = ICl\ (liquid) + 9{\cdot}8\ ;\ ICl\ (solid) + 12{\cdot}1.$$
$$I\ (gas) + Br\ (gas) = IBr\ (solid) + 11{\cdot}9.$$

This is another point of resemblance between cyanogen and the halogens. In the formation of cyanogen chloride, as well as in the combinations of the halogen elements with one another, there is hardly any other heat given off than that which corresponds to the change of state of the compound, *i.e.* to the conversion of the gaseous body into liquid or solid.

6. *Substitution of chlorine for the cyanogen.* From the previous results we conclude that the simple substitution of chlorine for hydrogen in gaseous hydrocyanic acid—

$$Cl + HCN\ (gas) = CNCl\ (gas) + H,$$

would absorb − 6·2. Such a reaction is therefore impossible, unless accompanied by the formation of secondary products, furnishing supplementary energy. On the contrary, the simple substitution of chlorine for the cyanogen—

$$Cl + HCN\ (gas) = HCl\ (gas) + CN\ (gas),$$

would give off + 14·2.

Lastly, the simultaneous formation of cyanogen chloride and gaseous hydrochloric acid—

$Cl_2 + HCN\ (gas) = CNCl\ (gas) + HCl\ (gas)$, would give off + 15·8.

We see that this last formation answers to the maximum of heat disengaged. This reaction, in fact, is produced in preference to any other. It is all the more readily effected as the combination between the cyanogen chloride and hydrochloric acid gives off a fresh quantity of heat, at least if the substances are in the liquid state, which again acts in the same way. However, the effects of these direct reactions between chlorine and free hydrocyanic aeid are complicated by various secondary reactions which are imperfectly understood. The direct reactions become more obvious, if we are operating on cyanides, the corresponding bodies being always considered in comparable forms:

$KCN\ (solid) + Cl_2\ (gas) = KCl\ (solid) + CNCl\ (gas)$ would give off + 39·0.

$\frac{1}{2}[Hg(CN)_2\ (solid) + 2Cl_2\ (gas) = HgCl_2\ (solid) + 2CNCl\ (gas)]$ gives off + 21·3.

All these quantities of heat are positive. The formation of

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liquid cyanogen chloride, together with mercuric chloride, gives off + 7·3 more; or, altogether, + 29·6. If we suppose the mercuric cyanide to be in solution, as well as the cyanogen chloride, these figures do not vary to any appreciable extent. The number + 27·5, instead of + 29·6, was found by experiment.

7. We must also note the *action of water* on cyanogen chloride. Water first dissolves it, and then slowly converts it into carbonic acid and ammonium chloride; a reaction similar to that in the case of amides. According to calculation—

$$CNCl\ (liquid) + 2H_2O\ (liquid) = CO_2\ (gas) + NH_4Cl\ (in\ solution) + 55{\cdot}9.$$

$$CNCl\ (gas) + 2H_2O\ (solid) = CO_2\ (gas) + NH_4Cl\ (solid) + 65{\cdot}4.$$

8. *The heat of combustion* of cyanogen chloride would be as follows:—

$$CNCl\ (gas) + O_2 = CO_2 + N + Cl + 129{\cdot}7.$$

We know that this combustion does not take place directly.

§ 11. Cyanogen Iodide.

1. This substance was synthetically prepared from pure potassium cyanide in aqueous solution (1 eq. = 6·5 litres) and solid iodine. The reaction is easy and rapid. In a first experiment, potassium cyanide was used, which had been prepared beforehand and proved to be pure. It was found that

$$KCN\ (1\ eq. = 6{\cdot}5\ litres) + I_2\ (solid) = CNI\ (in\ solution) + KI\ (in\ solution) + 6{\cdot}36\ Cal.$$

In a second experiment, pure hydrocyanic acid was used, of which a certain weight was dissolved in a diluted equivalent of potash, so as to give a solution containing KCN (1 eq. = 2 litres). On the addition of a corresponding quantity of solid iodine, the value, + 6·21 Cal., was obtained. We will adopt the average, + 6·3.

2. *Solution in water.* The solution in water of crystallised cyanogen iodide (6·3 grms. to 500 cc. of water) absorbs, at 20°, − 2·78.

3. *Formation from the elements.*

Initial system: K + C (diamond) + N + I_2 (solid) + water.
Final system: CNI (in solution) + KI (in solution).

First Step.

K + C (diamond) + N = KCN (solid)							+ 30·3
Solution	...	...	...	...	...	...	− 2·9
Reaction of I_2 (solid)			...	...	...	...	+ 6·3
				Sum	...	...	+ 33·7

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SECOND STEP.

K + I (solid) = KI (in solution)	+ 74·7
C (diamond) + N + I (solid) = CNI (in solution) ...	x
Sum ...	+ 74·7 + x

$$x = -41;$$

a value which applies to cyanogen iodide in solution. For solid iodide, we get—

C (diamond) + N + I (solid) = CNI (solid), − 38·2.

4. *Union of iodine with cyanogen.*

CN + I (solid) = CNI (solid) + 0·9.
CN + I (gas) = CNI (solid) + 6·3.

These values are very little less than that of the heat of formation of liquid cyanogen chloride, or + 9·9. They are less than the values relating to solid iodine chloride (+ 12·1) and to solid iodine bromide (+ 1·9). The difference, however, is not very great; another confirmation of the general analogy of all these components (see p. 338).

5. *Substitution.* The substitution of iodine for the hydrogen of hydrocyanic acid, with the simultaneous formation of hydriodic acid and cyanogen iodide—

HCN (gas) + I_2 (solid) = CNI (solid) + HI (gas), would absorb − 13·1.

Thus this reaction does not take place in a direct manner. But, on the contrary, we note the action of iodine on cyanides, which takes place owing to the extra energy, due to the action of the alkaline iodide. This is the calculation, all the bodies being brought to a similar state—

KCN (solid) + I_2 (solid) = KI (solid) + CNI (solid) ...	+ 13·3 Cal.
AgCN (solid) + I_2 (solid) = AgI (solid) + CNI (solid) ...	+ 11·6 „
$\frac{1}{2}$[$Hg(CN)_2$ (solid) + $2I_2$ (solid) = HgI_2 (solid) + 2CNI (solid)]	+ 6·0 „

Here, it may be repeated, there is disengagement of heat due to the formation of the metallic iodide: which formation is necessary in order to ensure the combination between the cyanogen and iodine.

6. It had already been found convenient to study the thermal formation of cyanogen bromide from bromide and dissolved potassium cyanide, but this formation is almost immediately followed by secondary reactions, which are indefinitely prolonged and cast a doubt on the numerical results observed at first. Therefore it was thought advisable to suppress them.

§ 12. POTASSIUM CYANATE.

1. Pure potassium cyanate was decomposed by means of dilute hydrochloric acid. If a quantity of water is used,

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sufficient to keep the whole of the carbonic acid formed in solution, the decomposition is complete at the end of a few minutes:

$$KCNO \text{ (in solution)} + 2HCl \text{ (in solution)} + H_2O = CO_2 \text{ (in solution)} + KCl \text{ (in solution)} + NH_4Cl \text{ (in solution)}.$$

This reaction gives off, according to the experiment performed, + 28·8 Cal.

2. On the other hand, the *solution of potassium cyanate*, KCNO (1 part of salt to 300 parts of water), absorbs − 5·2.

3. *Formation of potassium cyanate from the elements.* This is deduced from the above data.

Initial system:

$$K + C \text{ (diamond)} + N + 2H_2 + O_2 + Cl_2.$$

Final system:

$$CO_2 \text{ (in solution)} + KCl \text{ (in solution)} + NH_4Cl \text{ (in solution)}.$$

First Step.

$C + O_2 = CO_2$	− 94·0
Solution	+ 5·6
$K + Cl = KCl$ (in solution) ...	+ 100·8
$N + H_3 = NH_3$ (in solution) ...	+ 21·0
$H + Cl = HCl$ (in solution) ...	+ 39·3
$HCl + NH_3 = NH_4Cl$ (solution) ..	+ 12·45
	+ 273·15

Second Step.

$K + C + N + O = KCNO$ (solid)	x
Solution	− 5·2
$2(H + Cl) = 2HCl$ (diluted) ...	+ 78·6
$H_2 + O = H_2O$	+ 69·0
	+ 142·4 + x
Reaction ...	+ 28·8
	+ 171·2 + x

$$x = 273{\cdot}15 - 171{\cdot}2 = + 102.$$

Thus, the *formation of solid potassium cyanate from the elements*, $K + C$ (diamond) $+ N + O = KCNO$, gives off + 102·0. If the salt is in solution, + 96·8.

This same formation, from diluted potash—

$\frac{1}{2}[C_2 + N_2 + O + K_2O$ (diluted) $= 2KCNO$ (in solution)], gives off + 15·5.

From gaseous cyanogen—

$CN + K + O = KCNO$ (solid)	+ 139·3
$\frac{1}{2}[(CN)_2 + O + K_2O$ (diluted) $= 2KCNO$ (in solution)] ...	+ 51·8
$CN_2 + K_2O$ (diluted) $= KCNO$ (diluted) $+ KCN$ (diluted)	+ 34·2

4. All these values exceed the heats disengaged in the analogous reactions of the halogen elements properly so called.

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For example—

Cl_2 (gas) + K_2O (diluted) = KClO (diluted) + KCl (in solution) gives off only + 25·4.

There is, besides, the difference that the complex nature of cyanogen and its tendency either to form polymeric compounds and other condensed bodies, or to reproduce ammonia and its derivatives, gives rise to a number of secondary reactions, which are not observed in the case of chlorine. These reactions take place all the more readily in proportion as the heat disengaged by the direct reaction is itself greater, and therefore furnishes a greater reserve of energy for other transformations.

5. The union of dry potassium cyanide with gaseous oxygen, to form solid cyanate—

KCN(solid) + O (gas) = KCNO (solid), would give off + 102 − 30·3 = + 71·7;

a very high value, being nearly three-quarters of the heat (+ 94·0) disengaged in the combustion of the carbon contained in the cyanide.

These figures relate to the bodies when considered in their actual state; under which condition, up to the present, the absorption of oxygen by potassium cyanide has not been observed, perhaps because it has not been looked for. On the contrary, if the potassium cyanide be in the melted state, the absorption takes place easily, as we know. Now, the values which have just been calculated may be applied approximately, at a high temperature, to the same bodies in the known conditions of their actual reactions; for the melting of the cyanide and that of the cyanate must absorb quantities of heat which are little different. As regards the heat disengaged by the oxidation of its potassic compound, cyanogen resembles iodine, but, on the contrary, differs from chlorine. In fact, we get—

$KCl + O_3 = KClO_3$ (solid) absorbs	...	...	− 11
$KBr + O_3 = KBrO_3$ (solid) „	...	...	− 11·1
$KI + O_3 = KIO_3$ (solid) gives off	...	...	+ 44·1
KCN + O = KCNO (solid) gives off	...	...	+ 71·7

a progression which is the reverse of that which characterises the union of the same metal, such as potassium, with the same series of halogen bodies, such as chlorine (+ 105·0), gaseous bromine (+ 100·4), gaseous iodine (+ 85·4), and cyanogen (+ 67·6).

We can understand, from the above figures, why potassium cyanide shows such a great tendency to become oxidised, either under the influence of oxidising agents, or even under the influence of the air.

The combustible nature of one of the elements contained in cyanogen is, besides, opposed to its forming the peroxygenated

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acids which are produced in the case of chlorine and the halogen elements; such compounds would have too great a tendency to be converted into carbonic acid.

The total combustion of potassium cyanate in the solid state—

$\frac{1}{2}[2KCNO + O_3 = K_2CO_3 + CO_2 + N_2]$, would give off + 83·9.

6. The facility with which potassium cyanate is converted into ammonia, even by the simple fact of its prolonged contact with water, is easily explained; for—

$\frac{1}{2}[2KCNO \text{ (in solution)} + 4H_2O = K_2CO_3 \text{ (in solution)} + (NH_4)_2CO_3 \text{ (in solution)}]$, gives off + 20 Cal.

This is again a reaction of amides.

The well-known conversion of melted potassium cyanate, by means of aqueous vapour, into melted potassium carbonate, carbonic acid and ammonia gas, gives off about + 9 Cal.

The change of potassium cyanide under the united influence of oxygen and aqueous vapours at a high temperature into carbonate and ammonia—a change which is so pernicious in the industrial preparation of the prussiates—is as easily explained by thermo-chemistry. In fact, we should get, at the ordinary temperature—

$\frac{1}{2}[2KCN \text{ (solid)} + O_2 + 3H_2O \text{ (gaseous)} = K_2CO_3 \text{ (solid)} + CO_2 \text{ (gas)} + 2NH_3 \text{ (gas)}] + 79·3.$

Towards a red heat this value should still keep the same, as the cyanide and the carbonate are similarly fused.

A rapid resume has been made of the more immediate deductions from the new values relating to the heat of formation of cyanogen, hydrocyanic acid, and cyanides. It would be easy to develop and extend these conclusions to innumerable other reactions, the subject being most fruitful. Any one can do this as far as he deems expedient or interesting. The general table of the thermal formation of the cyanogen compounds will be found on p. 132.

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CHAPTER XII.

HEAT OF FORMATION OF THE SALTS PRODUCED BY THE OXYGENATED COMPOUNDS OF CHLORINE AND OTHER HALOGEN ELEMENTS.

§ 1. General Notions.

Chlorine and the halogen elements form with oxygen a series of compounds analogous with the oxygenated compounds of nitrogen, and which comprise even an additional member, viz. perchloric acid. Most of these compounds are energetic oxidising agents, either in the wet or in the dry way, and some of their salts (especially the chlorates) play an important part in the manufacture of explosive substances. This circumstance, therefore, makes it desirable to measure their heat of formation.

§ 2. Thermal Formation of Chloric Acid and Chlorates.

1. The thermal formation of chloric acid and chlorates has been already examined by Favre, Frankland, and Thomsen, but with very different results.

Favre [1] tried to measure the heat liberated in the action of gaseous chlorine on concentrated potash; according to him, the union of chlorine and oxygen to form chloric acid—

$$\tfrac{1}{2}[H_2O + Cl_2 + O_5 + \text{water} = H_2O, Cl_2O_5 \text{ (diluted)}],$$

would absorb − 65·2 Cal. The decomposition of solid potassium chlorate into oxygen and potassium chloride—

$$KClO_3 = KCl + O_3, \text{ would then liberate } + 64{\cdot}9.$$

But the learned author's calculation is complicated, and is based on uncertain data, such as the supposed insolubility of the salts formed in the alkaline solution.

Frankland,[2] having oxidised various organic substances, some

[1] "Journal de Pharmacie et de Chimie," 3e série, tom. xxiv. p. 316. 1853.
[2] "Philos. Magazine," vol. xxxii. p. 184. 1866.

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with free oxygen, others with potassium chlorate, found in three trials that the excess of heat developed by 9·75 grms. of potassium chlorate amounted to 378, 326, and 341, respectively; or, taking the average, to 348 Cal., which would give for

$$KClO_3 (= 122{\cdot}6 \text{ grms.}) + 4{\cdot}37 \text{ Cal.},$$

a value subject to the doubts involved by such an indirect determination.

Finally, Thomsen[1] reduced a diluted solution of chloric acid by means of sulphurous acid—an operation which can be easily carried out in a calorimeter; on the other hand, he decomposed potassium chlorate by means of the heat produced by the combustion of hydrogen—a process which does not seem to admit of such accuracy as the former one.

He deduced from his trials the following results:—

$$\tfrac{1}{2}[H_2O + Cl_2 + O_5 + \text{water} = H_2O, Cl_2O_5 \text{ (diluted)}], \quad -10{\cdot}2$$
$$KClO_3 \text{ (solid)} = KCl \text{ (solid)} + O_3, \quad +9{\cdot}8.$$

2. The following are the results arrived at by the author. Following the method he constantly adopted, he took, to start with, a *crystallised and definite salt*, in preference to a *titrated solution*, or a solution containing the acid prepared by precipitation — solutions whose composition is always less exact. Barium chlorate was used, which was in very fine crystals, and corresponded to the formula $Ba(ClO_3)_2 + H_2O$. Analysis of this salt gave—

	$BaSO_4$	H_2O
Found	72·2	5·7
Calculated	72·3	5·6

This salt, when dehydrated and then heated in a tube, is immediately decomposed with a very marked incandescence, and a kind of explosion which throws off to some distance a white powder, consisting of barium chloride; these effects are observed even when only a few grammes of the dry salt are operated upon. It is well known that analogous phenomena may be observed with potassium chlorate, but barium chlorate exhibits them to a far greater degree. This proves that its decomposition is exothermal.

3. A known weight, 2·5 grms., of this salt was dissolved, in one case in 400 cc., in another in 900 cc. of water, and reduced by means of 100 cc. of a moderately concentrated solution of sulphurous acid. The barium chlorate is thus completely converted into barium sulphate and hydrochloric acid, as was ascertained by various determinations. The reduction is effected more rapidly according as the solution is less diluted, all other things being equal. With 500 cc. of liquid, and 2·5

[1] "Journal fur Praktische Chemie," Band xi. s. 138. 1875.

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grms. of salt, at 12·5°, it lasted six to seven minutes; with 1000 cc., and the same weight of salt, it lasted fourteen to fifteen minutes. At 22° the duration of the reactions was found to differ but little; which proves that the preceding difference does not depend on the unequal heating produced by the reaction (6·5° in the first trial, 3·2° in the second). The sulphurous acid should be considerably in excess; when operating with only a very slight excess, the reaction effected at 23° lasted nearly twenty minutes, instead of seven.

All these durations of the reactions can be clearly defined according to the movement of the thermometer compared with the rate of cooling of a similar liquid of the same weight, and brought to the same heat, but in which no chemical reaction is produced.

4. For the reaction

$$\tfrac{1}{2}[Ba(ClO_3)_2 \text{ dissolved} + 6SO_2 \text{ (dissolved)} = BaSO_4 \text{ (precipitated)} + 2HCl \text{ (dilute)} + 5H_3SO_2 \text{ (dilute)}],$$

the following quantities of heat were obtained:—

Initial temperature.	Weight of salt.	Heat liberated for equivalent weights.
23° ...	2·500 $Ba(ClO_3)_2 + H_2O$ ...	213·8 Cal.
23° ...	2·500	215·2 „
22° ...	1·544 $Ba(ClO_3)_2$ anhydrous ...	215·2 „ (2 trials)
12° ...	2·500 $Ba(ClO_3)_2 + H_2O$ ...	214·3 „
12° ...	2·500 $Ba(ClO_3)_2 + H_2O$ ...	212·3 „
At 19° we should have, on an average ...		214·3 „

On the other hand, direct trials gave for the heat liberated by the action of dilute sulphuric acid on barium chlorate taken with the same degree of dilution as in the preceding experiments—

$$\tfrac{1}{2}[H_2SO_4 \text{ dilute} + Ba(ClO_3)_2 \text{ (dissolved)}], \text{ at } 19°, + 4·6;$$

whence we obtain for the union of dilute chloric acid with baryta—

$$\tfrac{1}{2}[2HClO_3 \text{ (dilute)} + BaO \text{ (dissolved)}] + 13·8;$$

and for the reduction of free chloric acid—

$$\tfrac{1}{2}[2HClO_3 \text{ (dilute)} + 6SO_2 \text{ (dissolved)} = 6H_2SO_4 \text{ (dilute)} + 2HCl \text{ (dilute)}] \text{ liberates } + 214·3 - 4·6 = + 209·7.$$

5. Let us note now the following data:—

$\tfrac{1}{2}[SO_2$ (dissolved) $+ 2H_2O + Cl_2$ (gas) $= H_2SO_4$ (dilute) $+ 2HCl$ (dissolved)] liberates	+ 36·95[1]
$H + Cl = HCl$ (dilute)	+ 39·3
$\tfrac{1}{2}[H_2 + O = H_2O$ (dilute)]	+ 34·5

[1] Thomsen.

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We deduce from these numbers—

$\frac{1}{2}[SO_2$ (dissolved) + O (gas) + $H_2O = H_2SO_4$ (dilute)] + 32·15;

and consequently—

$\frac{1}{2}[H_2O + Cl_2 + O_5$ + water = H_2O, Cl_2O_5 (dilute)] − 12·0.

This number depends on the heats of formation of water, hydrochloric and sulphuric acids.

6. Hence it is that the formation of dilute chloric acid from its elements—

$\frac{1}{2}[Cl_2 + O_6 + H_2$ + water = H_2O, Cl_2O_5 (dilute)], liberates + 22·5.

The conversion of dilute chloric acid into dilute hydrochloric acid and gaseous oxygen—

$HClO_3$ (diluted) = HCl (diluted) + O_3, liberates + 16·8.

This value plays an important part in oxidations.

7. It is the same for dissolved chlorates, decomposed into chlorides and free oxygen; for the heat liberated in the action of various bases on hydrochloric and chloric acids is essentially the same. In fact, the following numbers were found at 19°:—

	$\frac{1}{2}$[2HCl (diluted)]			$\frac{1}{2}$[2$HClO_3$ (diluted)]		
+ $\frac{1}{2}$[K_2O (diluted)]	...	...	+ 13·7	...	...	+ 13·7
+ $\frac{1}{2}$[Na_2O (diluted)]	...	...	+ 13·7	...	...	+ 13·7
+ $\frac{1}{2}$[BaO (diluted)]	...	...	+ 13·85	...	...	+ 13·8

8. Returning to the heats of solution of chlorides and chlorates, the values of which have been given elsewhere,[1] we obtain the heat of decomposition of chlorates into chlorides and oxygen (referred to the ordinary temperature)—

$KClO_3$ (solid) = KCl (solid) + O_3 + 11·0;

instead of + 9·8, given by Thomsen. These values are very near each other. It was also found that

$NaClO_3$ (solid) = NaCl (solid) + O_3 + 12·3.

$\frac{1}{2}[Ba\ (ClO_3)_2$ (solid) = $BaCl_2$ (solid) + $3O_2$] + 12·6.

Even at the temperature of the reactions, that is to say, at 500° or 600°, the quantities of heat, for *solid* salts, are nearly the same, as may be established by calculation. For instance, the specific heat of potassium chlorate for the equivalent weight $KClO_3$ is equal to 23·8; for KCl + O_3, the sum of the specific heats amounts to 23·3. The term U − V, which expresses the variation of the heat of combination, is therefore equal to

+ 0·5 cal. (T − *t*);

or, for an interval between zero and 500°, 0·25 Cal., which is an insignificant increase in comparison with + 11·0.

[1] "Annales de Chimie et de Physique," 5e série, tom. iv. pp. 103. 104.

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It follows from these numbers that combustion *effected by solid potassium chlorate* liberates more heat than the same combustion effected by means of free oxygen; viz. by + 1·83 Cal. for each equivalent of oxygen (O = 8) consumed (p. 134).

9. *The formation of chlorates from the elements*—

$$K + Cl + O_3 = KClO_3 \text{ (solid) liberates } + 94{\cdot}6 \text{ Cal.}$$
$$Na + Cl + O_3 = NaClO_3 \text{ (solid) liberates } + 85{\cdot}4 \text{ Cal.}$$

These quantities scarcely vary with the temperature; at least when the metals are solid. In fact, the specific heat of the system of elements, K + Cl + O_3, is 21·3; heat of the compound $KClO_3$ is 23·8. We have then U − V = − 2·5 cal. (T − *t*), or, what is the same thing, − 0·0025 Cal. (T − *t*), if we adopt the same unit as for the formation of chlorates. An interval of 100°, then, only produces an increase of − 0·25 Cal. in the heat liberated.

10. *Various reactions.* The action of gaseous chlorine on diluted potash may be considered as forming either hypochlorite, or chlorate, or free oxygen.

(*a*) With hypochlorite—

$$6Cl + 3K_2O \text{ (diluted)} = 3KClO \text{ (dissolved)} + 3KCl \text{ (diluted)}.$$

According to the experiments performed,[1] the reaction liberates

$$+ 25{\cdot}4 \times 3 = + 76{\cdot}2.$$

With soda, we have, + 75·9; with baryta, + 75·8.

(*b*) This reaction may also form chlorate—

$$6Cl + 3K_2O \text{ (diluted)} = KClO_3 \text{ (dissolved)} + 5KCl \text{ (dilute)},$$

which liberates, with potash, + 94·2; with soda, + 94·2; with baryta, + 95·0.

(*c*) The formation of potassium perchlorate and chloride, referred to the same weight of chlorine as the preceding—

$$\tfrac{3}{4}[8Cl + 4K_2O \text{ (diluted)} = 7KCl \text{ (dissolved)} + KClO_4 \text{ (dissolved)}], \text{ liberates } + 111{\cdot}0.$$

With soda, + 111·0; with baryta, + 111·8.

(*d*) Finally, the same reaction may develop chloride and free oxygen—

$$6Cl + 3K_2O \text{ (diluted)} = 6KCl \text{ (dissolved)} + O_3,$$

which liberates, with potash, + 111·0; with soda, + 110·0; with baryta, + 111·8.

It follows from these numbers that the formation of the hypochlorite corresponds to the least liberation of heat; then comes the chlorate, and finally the perchlorate and free oxygen, which liberate the most heat, the two quantities being, moreover,

[1] "Annales de Chimie et de Physique," 5ᵉ série, tom. v. pp. 335, 337, 338.

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sensibly the same. When hypochlorite is changed into chlorate—

$$3KClO \text{ (dissolved)} = KClO_3 \text{ (dissolved)} + 2KCl,$$

heat is liberated to the amount of

+ 18·0, for potassium salts; + 18·3, for sodium salts; + 19·9, for barium salts.

The second decomposition, that of the dissolved chlorate into chloride, liberates + 16·8 for the three salts as before stated.

The conversion of dissolved chlorate into perchlorate liberates sensibly the same quantity of heat.

It is seen that the relative stability of the solutions keeps increasing from the hypochlorite to the chlorate, then to the perchlorate and to free oxygen, which is consistent with what we know from chemistry.

Finally, if we refer the actions to the formation of the acids themselves, which gives at least the heat liberated by their union with the bases, we have—

$6Cl + 3H_2O$ + water = 3HClO (diluted) + 3HCl (diluted) liberates	+ 5·7
$6Cl + 3H_2O$ + water = $HClO_3$ (diluted) + 5HCl (diluted) liberates	+ 12·0
$\frac{1}{4}[8Cl + 4H_2O$ + water = $HClO_4$ (diluted) + 7HCl (diluted)] liberates	+ 28·9
$6Cl + 3H_2O$ + water = O_4 (gas) + 6HCl (diluted) liberates ...	+ 28·8

The thermal relations, therefore, remain the same.

11. *Successive degrees of oxidation.* Let us now examine the heats of formation of the different acids of chlorine.

From the experiments performed—

$\frac{1}{2}[H_2O + Cl_2 + O_2$ + water = H_2O, Cl_2O_2 (dilute)] absorbs ...	− 2·9
$\frac{1}{2}[H_2O + Cl_2 + O_5$ + water = H_2O, Cl_2O_5 (dilute)] absorbs	− 12·0
$\frac{1}{2}[H_2O + Cl_2 + O_7$ + water = H_2O, Cl_2O_7 (dilute)] liberates	+ 4·9

There is then, in the first place, an *absorption of heat which increases according as the proportion of oxygen united to equal weights of chlorine increases in the compound;* this is the case for the first two compounds.

But, on the contrary, heat is liberated in the case of the third, to the extent of + 16·9 for O; formation of perchloric acid.

The same relations subsist if we take oxygen as the unit and vary the chlorine. For a given weight of oxygen, such as $\frac{1}{2}[O_5] = 40$ grms., united to Cl = 35·5 grms. in dissolved chloric acid, there is an absorption of − 12·0. The same weight of oxygen, when united to $Cl_5 = 177·5$ in dissolved hypochlorous acid, gives rise to an absorption of

$$-2·9 \times 5 = -14·5,$$

which is more considerable. But this increase in the heat absorbed does not extend to perchloric acid; it, on the contrary,

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gives rise to a liberation of heat of + 3·5, for the same weight of oxygen.

These relations are the more remarkable in the acids of chlorine, since the formation of successive combinations of one and the same element with oxygen generally liberates heat, as is shown by the history of the oxygenated combinations of sulphur, selenium, phosphorus, arsenic, etc.

12. Nevertheless, similar anomalies are found in the study of the combinations of iodine and nitrogen with oxygen. In fact, if we compare hypoiodous, iodic, and periodic acids, $\frac{1}{2}[I_2 + O +$ water $= I_2O$ (in solution)] absorbs, according to the author's experiments, a quantity of heat notably superior, in absolute value, to − 5·2.

$\frac{1}{2}[I_2 + O_5 +$ water $= I_2O_5$ (dissolved)] liberates	...	+ 21·5 (Thomsen)
or	...	+ 22·2 (Berthelot)
$\frac{1}{2}[I_2 + O_7 +$ water $= I_2O_7$ (dissolved)] liberates	...	+ 13·5 (Thomsen)

Hence it is seen that the heat liberated presents a minimum and a maximum, neither of which corresponds to the highest degree of oxidation. The combinations of nitrogen and oxygen present an analogous minimum for nitric oxide (p. 84). These numbers are given here in order to show how difficult it is to generalise the relations between the quantities of heat disengaged or absorbed, and the multiple proportions of the successive combinations of two elements.

If the minimum of heat liberated or the maximum of heat absorbed corresponded in all cases to the first term formed by the successive union of two elements, and if the heat liberated then increased regularly with the proportion of the variable element, it might be supposed that one of the elements—the one considered as constant—undergoes a special isomeric modification preceding the combination, and from which, as a starting-point, the quantities of heat should be reckoned. But it seems difficult to admit this hypothesis in the oxygenated series of nitrogen, iodine, and even chlorine, series in which the thermal minimum and maximum correspond neither to the first nor to the second degree of oxidation.

13. It was thought desirable to pursue the comparison further, and to extend it to chlorous acid. To this end it was attempted to prepare a definite salt, barium chlorite, which, according to Millon, should be a crystallised salt. By closely following the author's instructions, a crystallised salt was obtained, presenting a scaly appearance—as he says—and giving by analysis numbers which essentially correspond to the formula $Ba(ClO_2)_2$; but a closer examination showed that the salt was nothing but a mixture of barium chloride and perchlorate in equivalent proportions (with a small percentage of chlorite)—

$$BaCl_2 + Ba(ClO_4)_2.$$

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This substance presents the same percentage composition as the chlorite. It appears that its formation in the action of chlorous acid on the alkalis must account for the discoloration of the solution which takes place, as is known, after some time.

§ 3. Thermal Formation of Perchloric Acid and its Salts.

1. The result of the researches made on the oxyacids of chlorine and other halogen elements led to the study of the heat of formation of perchloric acid; the results, which are with great difficulty obtained, demonstrate a certain number of new chemical facts. They show at the same time how thermochemistry explains the differences of stability and activity which exist between pure perchloric acid and the same acid when combined with a more considerable quantity of water.

2. In fact, it is known, principally from the researches of Roscoe,[1] that there exist several hydrated perchloric acids, namely, monohydrated acid, properly so called, or $HClO_4$, a crystallised hydrate, $HClO_4H_2O$, and a hydrate, $HClO_42H_2O$, volatile at 200°, and partly dissociable, even under the conditions of its distillation.

These experiments were reproduced; it was even succeeded in obtaining the first acid in the crystallised form. It suffices to take the liquid acid, which contains a slight percentage of water in excess, and to place it in a cooling mixture. The acid becomes crystallised, and the mother-liquid is decanted. It is allowed to liquefy, and then recrystallised, which finally gives an acid fusible at 15°, a point of fusion which is still not high enough. Its composition was proved by analysis. It is a body which eagerly absorbs water and emits dense fumes on contact with the air.

3. The solution of monohydrated liquid $HClO_4$, at 19°, in one hundred times its weight of water, liberates + 20·3 Cal. This is rather a delicate experiment, owing to the rapidity with which the acid attracts moisture while being weighed, and also to the violence with which it reacts on the water at the time of the calorimetric part of the experiment. The preceding figure is enormous; it exceeds the heat of solution of all ordinary monohydrated acids—being, for instance, more than double that of hydrated sulphuric acid, H_2SO_4. It is even nearly equal to the heat of solution of anhydrous sulphuric acid (+ 18·7) and anhydrous phosphoric acid (+ 20·8), which are the highest hitherto known; but they refer to anhydrous bodies. The figure + 20·3 also exceeds the heats of solution of hydracids, although the latter are increased from 6 Cal. to 8 Cal., owing to their gaseous state.

This enormous heat of hydration of perchloric acid explains

[1] "Annalen der Chemie und Pharmacie," Band cxxxi. s. 376. 1861.

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the great difference which exists between the reactions of this acid when diluted with water—a condition under which it is almost as stable as dilute sulphuric acid—and those of the monohydrated acid, which ignites hydriodic acid gas, and acts with explosive violence on oxidisable bodies. This subject will be referred to again later on.

4. Monohydrated perchloric acid decomposes spontaneously, as Roscoe observed. It is at first colourless, but it assumes a yellow, then a red and brownish-red colour, and eventually liberates gases which render the containing vessels liable to burst; this is the more to be feared since the necks of emery flasks soon become stopped up through the formation of crystals of the second hydrated perchloric acid.

The acid which has suffered a partial decomposition is not suitable for measuring the heat of hydration on account of its becoming less and less considerable, owing to the formation of water which accompanies this decomposition. Notwithstanding this formation of water, the acidimetric value of the acid—referred to the equivalent weight of perchloric acid—does not fall, and it may even apparently increase a little, since the lower oxygenated acids of chlorine have an equivalent less than that of perchloric acid. This is a cause of error which should be noted.

5. A similar decomposition is produced under the influence of heat, and prevents the re-distillation of perchloric acid. It takes place in the very conditions of its preparation from potassium perchlorate and sulphuric acid, as is shown by the constant liberation of chlorine which accompanies the distillation. It appears that the monohydrated acid cannot be separated unless carried away in a current of gas; it is only obtained in small quantities. This depends on the fact that the decomposition of perchloric acid liberates heat. Even in its preparation from potassium perchlorate and concentrated sulphuric acid, the reaction, when once started by the action of an external source of heat, continues of itself, after the removal of this source, and sometimes with a violence sufficient to give rise to an explosion. This fact proves that the reaction is exothermal. At the same time, chlorine and oxygen are liberated, which carry away the perchloric vapour and render its condensation difficult.

6. Some details may now be given respecting the oxidising characters exhibited by perchloric acid.

In dilute solution, this acid is not reduced by any known body. No action is caused by sulphurous, hydrosulphuric, hydrosulphurous,[1] or hydriodic acid, by free hydrogen, zinc

[1] It was especially proved by accurate weighing, that this acid, which was recently declared capable of reducing perchlorates, does not act in reality except on the small quantities of chlorates often contained in perchlorates.

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in the presence of acids, sodium amalgam in the presence of pure acidulated or alkaline water, or by electrolysis. Perchloric acid and perchlorates in solution are even as stable as sulphates.

The hydrates $HClO_4$, $2H_2O$ (liquid) and even $HClO_4$, H_2O (crystallised), hydrates whose heat of solution only rises to + 5·3 Cal. for the former, and + 7·7 Cal. for the latter,[1] seem to be scarcely more active than the diluted acid itself, from determinations made with hydriodic gas, sulphurous acid, and arsenious acid.

Monohydrated perchloric acid acts quite differently; which can be explained by the fact that it also liberates + 20·3 Cal. in its solution. When brought into contact with oxidisable bodies it sometimes remains almost inactive just as in the case of nitric acid and iron (the passive state); on the other hand, it sometimes attacks them suddenly and with explosive violence. It causes the ignition of hydriodic acid and sodium iodide; it attacks arsenious acid, etc., very energetically. With hydrogenised bodies the formation of water modifies the action—by converting a portion of the acid into a higher hydrate. Arsenious acid does not present this disadvantage; it produces an oxychloride, intermediate between this body and arsenic acid, and to which reference has already been made while treating of the reciprocal displacements of oxygen and halogen bodies.[2] Nevertheless, it has been impossible to utilise this reaction for calorimetric measurements, even by dissolving these products in soda, owing to the uncertain constitution of the arsenic acid formed, which presents differences similar to those of the several phosphoric acids. Hence it is that the saturation of arsenic acid by soda liberates much less heat than that of normal arsenic acid. It is this fact that interferes with all the calculations.

7. It is only necessary to cite the following figures, which show the multiplicity of the simultaneous modes of decomposition of perchloric acid.[3] 1·175 grm. of this acid, in presence of a great excess of arsenious acid, was distributed in the following manner: 0·264 grm. yielded all its oxygen (O_4) to the arsenious acid; 0·139 grm. was destroyed in HCl + O_4, which fixed itself on the same acid; 0·145 grm. in Cl_2 + O_7 (fixed on the arsenious acid) + H_2O; 0·645 grm. left unchanged.

According to a special determination made, only a few milligrammes formed chlorous acid.

The heat liberated in the combination of perchloric acid with various bases, at 18°, was measured.

[1] About + 11·7 in the liquid state.

[2] "Annales de Chimie et de Physique," 5e série, tom. xv. p. 211.

[3] See pp. 6, 7.

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$\frac{1}{2}[2HClO_4$ (1 equivalent = 6 litres) + Na_2O (1 equivalent = 6 litres)] disengages ... ... + 14·25

$\frac{1}{2}[2HClO_4$ (1 equivalent = 6 litres) + 2 equivalent Na_2O (1 equivalent = 6 litres)] disengages ... ... + 0·07

$\frac{1}{2}[2HClO_4$ (1 equivalent = 6 litres) + BaO (1 equivalent = 6 litres)] disengages ... ... + 14·47

$\frac{1}{2}[2HClO_4$ (1 equivalent = 6 litres) + 2 equivalent BaO (1 equivalent = 6 litres)] disengages ... ... + 0·08

$HClO_4$ (1 equivalent = 6 litres) + NH_3 (1 equivalent = 4 litres) disengages ... ... + 12·90

$HClO_4$ (1 equivalent = 6 litres) + 2 equivalent NH_3 liberates ... + 0·00

Potash liberated the same quantity of heat as soda, but the potash solutions were taken twice as weak in order to avoid precipitation of the perchlorate.

The heat of solution of the perchlorate may now be added:

$KClO_4$ + water absorbs	...	...	− 12·1
$NaClO_4$ (at 100°) ...	...	...	− 3·5
$\frac{1}{2}[Ba(ClO_4)_2]$ at 100°	...	...	− 0·9
NH_4ClO_4 at 20° ...	...	...	− 6·36

8. Let us moreover examine *the heat of formation of perchloric acid and perchlorates from their elements.*

The author and M. Vieille determined the heat of formation of potassium perchlorate by mixing it in precisely equivalent proportions with a combustible substance, such as potassium or ammonium picrate, explosive in itself and therefore capable of giving rise to an instantaneous reaction. This same substance being burnt, on the other hand, by means of free oxygen, the difference between the two quantities of heat measured represents the excess of heat developed by the reaction by means of free oxygen over the heat developed by the reaction by means of combined oxygen: that is, the heat absorbed (or liberated) by the decomposition of potassium perchlorate into free oxygen and potassium chloride—

$$KClO_4 \text{ (solid)} = KCl \text{ (solid)} + 2O_2.$$

This quantity is derived from two experimental data only; it is independent of the heats of combustion of potassium, carbon, and hydrogen, as also of that of chlorination of potassium.

It was found each time that the weight of the potassium chloride formed (determined as silver chloride) was within $\frac{1}{200}$ of that which corresponded to the complete decomposition of the perchlorate. On the contrary, the combustion of the picrate was not found to be complete when the operations were conducted in an atmosphere of nitrogen; a certain deficit being noticeable in the carbonic acid, which is accounted for by the free carbon and carbon monoxide.[1] For this reason it was

[1] A corresponding fraction of the oxygen of the perchlorate is liberated owing to the simultaneous decomposition of this salt, but this in no way affects the calculation. Moreover, let us bear in mind that the combustion of potassium picrate converts the potash into bicarbonate, as was proved.

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deemed advisable to operate in an atmosphere of oxygen, which completes the combustion, as was proved by the determination of the carbonic acid.

Three series of experiments were made; namely, with potassium picrate, ammonium picrate, and picric acid; but only the first two gave satisfactory results, as the combustion of the picric acid was never complete, probably owing to its being, to a certain extent, volatile.

The numbers obtained with potassium picrate burnt, in the one case by pure oxygen, and in the other by perchlorate, differ by − 8·6 Cal.; the numbers obtained with ammonium picrate, by − 6·5 Cal.; results which agree as closely as could be expected for values which represent the difference of numbers that are far too high. We shall adopt the mean − 7·5 Cal. as corresponding to the reaction—

$$KClO_4 \text{ (solid)} = KCl \text{ (solid)} + 2O_2 \text{ gas.}$$

This decomposition, when effected at the ordinary temperature, would then absorb heat, contrary to what takes place in the decomposition of potassium chlorate, which liberates heat to the amount of + 11·0 Cal.

It is easy to calculate the heat of formation of potassium perchlorate from the elements. For, if we admit that

$K + Cl = KCl$ (solid) liberates	+ 105·0 Cal.
$K + Cl + O_4 = KClO_4$ (solid) liberates	+ 112·5 „

From this figure and the preceding data it follows that

$H + Cl + 2O_2 = HClO_4$ (liquid, pure) disengages	+ 19·1
$H + Cl + 2O_2$ + water = $HClO_4$ (diluted)	+ 39·35
$K + Cl + 2O_2 = KClO_4$ (solid) + 112·5 dissolved	+ 100·4
$Na + Cl + 2O_2 = NaClO_4$ (solid) + 100·2 dissolved	+ 96·7
$N + H_4 + Cl + 2O_2 = NH_4ClO_4$ (solid) + 79·7 dissolved ...	+ 73·3
$KClO_3 + O = KClO_4$ (solid)	+ 17·9

9. We derive from these figures—

$HClO_4$ (pure, liquid) = HCl (gas) + O_4 liberates	+ 2·9
$\frac{1}{2}[2HClO_4$ (pure, liquid) = $Cl_2 + O_7 + H_2O$ (gas)], + 9·9; H_2O (liquid)	+ 14·9
$HClO_4$ (diluted) = $HCl + O_4$	nil.
$\frac{1}{2}[2HClO_4$ (diluted) = $Cl_2 + O_7 + H_2O$ liquid)]	− 4·9

numbers which account for the difference between the stability of the concentrated and diluted acids, and also for the easy decomposition of the concentrated acid.

10. The perchlorates in solution are converted into chlorides with scarcely any thermal phenomenon, but it is different with the solid salts. In fact—

$KClO_4$ (solid) = KCl (solid) + $2O_2$	− 7·5
$NaClO_4$ (solid) = NaCl (solid) + $2O_2$	− 3·0
$\frac{1}{2}[Ba(ClO_4)_2$ solid = $BaCl_2$ (solid) + $4O_2]$ ...	− 1·1

The conversion of a solid perchlorate into chloride, at the ordinary temperature, therefore, absorbs heat; that is to say, it

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could not become explosive; whereas, according to the measurements made, the contrary is the case with chlorates.

The sign of the phenomenon, however, does not seem necessarily to change with elevation of temperature; the molecular heat of potassium perchlorate (26·3), for instance, being smaller than the sum of those of the chloride and oxygen (33·9); that is to say that, towards 400°, the divergence in absolute value would be increased by about 3 Cal.

11. The conversion of potassium chlorate into perchlorate is therefore exothermal, as might be foreseen.

At the ordinary temperature,

$$4KClO_3 \equiv 3KClO_4 + KCl \text{ would liberate } + 63.$$

This is, moreover, in conformity with the thermal relation already observed between the hypochlorites and chlorates, the latter being more stable than the former, but also being formed with a smaller absorption of heat.

12. The thermal relations also show that the decomposition of ammonium perchlorate must be explosive, for—

$$NH_4ClO_4 \text{ (solid)} \doteq Cl + O_2 + N + 2H_2O \text{ (liquid)} \quad \text{liberates } + 58{\cdot}3 \text{ Cal.}$$

$$NH_4ClO_4 \text{ (solid)} \doteq Cl + O_2 + N + 2H_2O \text{ (water as vapour)} \quad \text{liberates } + 38{\cdot}8 \text{ Cal.}$$

With the salt in a melted state we should have, in addition, the heat of fusion. This is verified by experiment. In fact, ammonium perchlorate, when heated, first melts; then the liquid becomes incandescent, assuming a spheroidal form; the brilliant bead thus produced is decomposed with great rapidity into free chlorine, oxygen and water, with the production of a yellowish flame. The salt does not, however, detonate; at least when only a small quantity is operated on. These phenomena resemble those of the decomposition of ammonium nitrate (*nitrum flammans*), but possess rather more intensity.

13. Reference has been already made to the great heat of solution (+ 20·3) of hydrated perchloric acid $HClO_4$, which is more than double that of all the other monohydrated acids, and is comparable to that of the most powerful anhydrous acids. The greatness of the heat liberated is followed up to the secondary hydrates.[1] That of the second hydrate,

$$HClO_4 \text{ (liquid)} + H_2O \text{ (liquid)} = HClO_4, H_2O;$$

liberates (the hydrate being solid) + 12·6 Cal.; and, if considered as a liquid, about + 8·6. The formation of the third hydrate—

$$HClO_4, H_2O + H_2O = HClO_4, 2H_2O \text{ (liquid)},$$

[1] With regard to the heat of dilution of perchloric acid, which presents some remarkable peculiarities, see researches made, "Annales de Chimie et de Physique," 5ᵉ série, tom. xxvii. p. 222.

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liberates also + 7·4; a value comparable to the heat of formation of the secondary hydrated sulphuric acid. These numbers tend to support the opinion that considered the hydrated perchloric acids as the last indication of the pentabasic character recognised in perchloric acid. Such a character would only declare itself by the formation of hydrates with an abundant liberation of heat, perchloric acid only forming monobasic salts. In another series—HRO_3—it has been shown already how to pass from monobasic chloric and nitric acids to tribasic phosphoric acid by means of iodic acid, which presents certain intermediate characters.[1]

We see by these details how thermo-chemistry accounts for the characteristic properties of perchlorates, and especially for the singular opposition which exists in the energetic oxidising reactions of the concentrated acid, and the great stability of the diluted acid.

§ 4. Oxygenated Compounds of Bromine.

1. The thermal formation of bromic acid, potassium bromate, and potassium hypobromite was studied.

2. Very pure potassium bromate was used, which had been prepared and analysed by the author himself.

It was dissolved in water.

$KBrO_3$ + water (1 part of salt + 50 parts of water), at 11°, absorbs − 9·85 Cal.

This solution was reduced by means of an aqueous solution of sulphurous acid; also the heat liberated by the union of the diluted bromic acid with the potash was measured; this is essentially the same as the heat of neutralisation of chloric, hydrobomic, and hydrochloric acids (+ 13·7) by the same base.

3. All calculations being made, it was found for *bromic acid* that—

$$\tfrac{1}{2}[Br_2\,(\text{liq.}) + O_5 + H_2O + \text{water} = H_2O, Br_2O_5\,(\text{diluted})]$$

absorbs − 24·8.

Thomsen, having reduced the same acid by means of stannous chloride, found − 21·8, but on substituting in the calculation of his experiments the number 38·5, which seems to be the more accurate,[2] for the number 38·0, which he adopted for the chlorination of stannous chloride, he also arrived at − 24·8.

From this we get—

$$\tfrac{1}{2}[Br_2\,(\text{gas}) + O_5 + H_2O + \text{water} = H_2O, Br_2O_5\,(\text{diluted})], - 20{\cdot}8\ ;$$

[1] "Annales de Chimie et de Physique," tom. xii. pp. 313, 314.

[2] Ibid., 5e série, tom. v. p. 330

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a number almost double that of the heat absorbed by the formation of chloric acid ($-12{\cdot}0$).

4. Again, for bromic acid (and bromates in solution)—

$$HBrO_3 \text{ (diluted)} = HBr \text{ (diluted)} + O_3, + 15{\cdot}5;$$

and for solid potassium bromate—

$$KBrO_3 \text{ (solid)} = KBr + O_3, + 12{\cdot}1;$$

values which are essentially the same as for chloric acid in solution ($+16{\cdot}8$) and for solid potassium chlorate ($+11{\cdot}0$).

Finally, from the elements—

$$K + Br \text{ (gas)} + O_3 = KBrO_3 \text{ (solid) liberates} + 89{\cdot}3.$$

5. *Hypobromous acid.*—The hypobromites are easily formed by the action of bromine on alkaline solutions.

It was found, in presence of an excess of alkali, the bromine being liquid, that—

Na_2O (1 equiv. = 3 litres) + Br (14·318 grms. and 3·365 grms.) at 9° + 6·0
K_2O (1 equiv. = 4 litres) + Br (15·801 grms. and 5·734 grms.) at 11° + 5·95
BaO (1 equiv. = 6 litres) + Br (12·096 grms. and 12·339 grms.) at 13° + 5·7

Admitting that diluted hypobromous acid, when combining with bases, liberates the same quantity of heat as hypochlorous acid; that is to say, + 9·5; it may be deduced from the preceding figures that—

$$\tfrac{1}{2}[Br_2 \text{ (liquid)} + O + \text{water} = Br_2O \text{ (diluted)}], - 6{\cdot}7;$$
$$\tfrac{1}{2}[Br_2 \text{ (gas)} + O + \text{water} = Br_2O \text{ (diluted)}], - 3{\cdot}1.$$

The latter number is essentially the same as what was observed for the formation of hypochlorous acid ($-2{\cdot}9$).

The alkalies, moreover, dissolve a greater quantity of bromine than that which corresponds to the formation of hypobromous acid. Thus baryta water dissolves in the cold nearly 2 eq. of bromine: or Br_4 for BaO. These facts are explained by the simultaneous formation of alkaline bromides[1] and of hypobromites.

Before pursuing these comparisons further, it is advisable to study the thermal formation of the oxygenated compounds of iodine.

§ 5. Iodic Acid and Iodates.

1. The results will be given which were obtained by the action of iodine on potash, by which are formed hypoiodous and iodic acids. It will then be convenient to examine the reaction of iodic acid on water and alkalies, and also finally to compare the thermal formation of the oxygenated salts derived from chlorine, bromine, and iodine, endeavouring at the same time to deduce therefrom some new data for molecular mechanics.

[1] "Annales de Chimie et de Physique," 5e série, tom. xxi. pp. 375, 378.

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2. If iodine be dissolved in diluted potash, at the ordinary temperature, with the aid of the crusher described in p. 247, two thermal effects succeed each other very rapidly. During the first minute a lowering of the temperature is observed, which reaches – 0·30° when we dissolve, for instance, 31 grms. of iodine in 500 cc. of a solution containing one quarter of an equivalent of potash per litre.

This initial phenomenon corresponds to the solution of the greater portion of the iodine employed. Effects of the same sign take place with solutions twice and four times as diluted. As soon as these effects are produced the thermometer begins to rise again in consequence of a new reaction, which lasts four to five minutes, while the whole of the iodine becomes dissolved. All the reaction can be effected with equivalent proportions (excepting a trace of free iodine or some other compound which turns the liquor slightly yellow). At this moment the solution contains potassium iodate and iodide, according to the well-known reaction—

$$3I_2 + 3K_2O \text{ (diluted)} = 6KI \text{ (dissolved)} + KIO_3 \text{ (dissolved)}.$$

3. It may be that the initial phenomenon is due to the formation of a hypoiodite—

$$I_2 + K_2O \text{ (diluted)} = KIO \text{ (diluted)} + KI \text{ (diluted)};$$

but this body has only a momentary existence, and is changed forthwith into iodate at the ordinary temperature.

4. It is well known that the same reaction with the hypochlorites is only produced very rapidly at 100°.

The hypobromite, with an excess of alkali, resists much longer, as has been proved.

5. This unequal stability of the three salts is explained by the inverse progression of the stability of the chlorates, bromates, and iodates, as will be seen by-and-by. Free hypochlorous acid is, on the contrary, the most stable of all; for it can be displaced unchanged when cold by carbonic acid, and even by acetic acid, whereas either of the latter acids, when in presence of the hypobromites, separate the bromine at once, as Ballard has observed from the beginning. This bromine is probably mixed with some other compound, as was ascertained from the measurement of the heat liberated.

6. Let us, however, return to the formation of the hypoiodite. When iodine is added to diluted potash in successive fractions—for instance, in twice or three times—each addition gives rise to the same succession of phenomena, namely, to a lowering of temperature, immediately followed by an increase of heat; which shows that the effect is very characteristic of the reaction itself, and independent of the fractions of iodine and potash already combined. These singular effects, which only the

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thermometer can reveal to us, require to be determined by figures:

½[I_2 + K_2O (1 equiv. = 2 litres)] at 14°—	
First effect: absorption	− 0·58
Second effect: liberation	+ 0·65
Total effect ...	+ 0·07
½[I_2 + K_2O (1 equiv. = 4 litres)] at 15°—	
Adding half the iodine: first effect	− 0·38
" " second effect	+ 0·30
Total effect ...	− 0·08
Adding the surplus of iodine: first effect ...	− 0·19
" " second effect ...	+ 0·17
Total effect ...	− 0·02
The total effect of the two effects united ...	− 0·10
½[I_2 + K_2O (1 equiv. = 8 litres)] at 15°—	
First effect	− 1·27
Second effect	+ 1·18
Total effect ...	− 0·09

Let us note here that the first thermal effect, namely, the cooling, does not afford an exact measure of the heat absorbed in the corresponding reaction (formation of hypoiodite), but only a superior limit, since the fresh rise in the temperature succeeds too rapidly.

7. It being admitted that the final product of the preceding reaction is potassium iodate in solution—

$$6I \text{ (solid)} + 3K_2O \text{ (diluted)} = KIO_3 \text{ (dissolved)} + 5KI \text{ (dilute)};$$

and also that the formation of diluted potassium iodide—

$$K + I + \text{water} = KI \text{ (diluted) liberates} + 74{\cdot}7 \text{ Cal.};$$

we pass from this to anhydrous iodic acid, monohydrated acid, and solid potassium iodate, by means of the following data:—

(*a*) *Potassium iodate in solution.*

½[$2HIO_3$ (1 equiv. = 1 litre) + K_2O (1 equiv. = 1 litre) = $2KIO_3$ (dissolved)], at 13°	+ 14·30
½[$2HIO_3$ (1 equiv. = 4 litres) + K_2O (1 equiv. = 4 litres) = $2KIO_3$ (dissolved)]	+ 14·25

These numbers slightly exceed the heat of neutralisation of nitric acid by potash. This excess was ascertained by the method of reciprocal double decompositions; that is, by treating alternately dissolved potassium iodate with diluted nitric acid, and potassium nitrate with iodic acid, in presence of the same quantities of water.

(*b*) *Solution of hydrated iodic acid.*

HIO_3 (crystallised) (1 part to 45 parts of water) + water, at 12°, − 2·67.

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Ditte found − 2·24, and Thomsen − 2·17, at a slightly different temperature.

(*c*) *Dilution of iodic acid.*

HIO_3 (1 equiv. = 1 litre) + its volume of water, at 13° ...	− 0·30
HIO (1 equiv. = 2 litres) + „ „ ...	− 0·08
HIO_3 (1 equiv. = 4 litres) + „ „ ...	− 0·0

(*d*) *Solution of anhydrous iodic acid.*—This body was prepared pure, and its composition ascertained by analysis.

$\frac{1}{2}[I_2O_5$ (1 part to 45 parts of water, at 12°) + water, − 0·81.

Ditte found − 0·95, and Thomsen − 0·89, at a slightly different temperature.

(*e*) *Solution of semihydrated iodic acid.*—This body is crystallised and well defined. The composition was ascertained.

$\frac{1}{2}[2HIO_3I_2O_5$ (1 part + 45 part of water, at 12°) + water, − 2·86.

(*f*) It was thought necessary to ascertain whether the three solutions formed by anhydrous, monohydrated, and semi-hydrated acid contain the acid in the same molecular state.

To this end, these solutions were treated, as soon as they were made, with potash (1 equiv. = 2 litres). They all liberated the same quantity of heat—

For $\frac{1}{2}[I_2O_5]$	+ 14·28
For HIO_3...	+ 14·31
$\frac{1}{2}[2HIO_3, I_2O_5]$	+ 14.35

(*g*) *Solution of the potassium iodates.*—Neutral iodate (crystallised)—

KIO_3 (crystallised) (1 part + 40 parts of water) + water, at 12°, − 6·05.

Dilution.

KIO_3 (1 equiv. = 2 litres) + its volume of water, at 13°, − 0·36
KIO_3 (1 equiv. = 4 litres) + „ „ „ − 0·0

Acid iodate (crystallised)—

KIO_3,HIO_3 (crystallised) (1 part + 40 parts of water) + water − 11·8

(*h*) *Formation of iodic acid from the elements.*—From the preceding data we deduce—

$\frac{1}{2}[I_2$ solid + 0_5 + water = H_2O, I_2O_5 diluted], + 22·6.

This number, obtained by the synthetical method, is consistent with the value + 21·5 found by Thomsen, by means of analytical processes.

We have, moreover—

$\frac{1}{2}[I_2 + O_5 = I_2O_5$ (anhydrous)]	+ 18·0 Cal.
$\frac{1}{2}[I_2$ (gas) + $O_5 = I_2O_5$ (solid)	+ 23·4 „
H + I + O_3 + water = HIO_3 (dissolved) ...	+ 57·1 „
H + I + O_3 = HIO_3 (crystallised)	+ 59·8 „
$\frac{1}{2}[H_2O$ (solid) + I_2O_5 (solid) = $2HIO_3$ (crystallised)]	+ 1·13 „

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According to the last number the hydration of the iodic acid does not liberate more heat than the hydrated salts do, and about the same quantity as anhydrous nitric acid.

We have also—

$\frac{1}{2}[I_2O_5$ (solid) + 2HIO (solid) = $2HIO_3, I_2O_5]$, + 0·62 ;
HIO (dissolved) = HI (dissolved) + O_3 (gaseous), − 43·9.

(*i*) *Salts.*

$\frac{1}{2}[I_2O_5 + K_2O = 2KIO_3$ (solid)]	+ 55·5
$\frac{1}{2}[I_2O_5 + BaO = Ba(IO_3)_2$ (solid)]	+ 34·9
HIO_3 (cryst.) + KHO (solid) = KIO_3 (cryst.) + H_2O (solid) ...	+ 31·5
$\frac{1}{2}[2HIO_3$ (cryst.) + $Ba(HO)_2$ (solid) = $Ba(IO_3)_2$ (solid) + $2H_2O$ (solid)]	+ 25·6

The formation of solid potassium iodate, shown by the above figure, liberates far less heat than the sulphate (+ 71·1, anhydrous substance; 40·7, hydrated substance) and potassium nitrate (+ 64·2, anhydrous; + 42·6, hydrated). On the contrary, it exceeds to a notable degree that of the monobasic organic salts, such as the acetate (+ 55·1, anhydrous; + 21·9, hydrated). It is, however, comparable to that of the salts of the most powerful organic acids, such as potassium oxalate (+ 29·4, see table, p. 127), or again, acid iodate—

KIO_3 (crystallised) + HIO_3 (solid) = KIO_3, HIO_3 (solid), + 3·1,

the value of the class of ordinary double salts. We have finally from the elements—

K + I (solid) + O_3 = KIO_3 (solid)	+ 123·9
With I (gas)	+ 129·3
KIO_3 (solid) = KI (solid) + O_3	− 44·1
KIO_3 (in solution) = KI (in solution) + O_3 ...	− 43·4

8. The heat liberated by the formation of solid potassium iodate from the elements (+ 129·3) exceeds that of the solid bromate and chlorate. In fact, it was found that—

K + Cl + O_3 = $KClO_3$ disengages	+ 94·6
K + Br (gas) + O_3 = $KBrO_3$ disengages ...	+ 87·6
K + I (gas) + O_3 = KIO_3 disengages ...	+ 129·3

It is well known that the relative stability of the three salts goes on increasing from the bromate to the chlorate and then to the iodate. This becomes still more evident by the comparison of the heat brought into play when the three solid salts are decomposed, with the liberation of oxygen.

$KClO_3$ = KCl + O_3 disengages	+ 11·0
$KBrO_3$ = KBr + O_3 „	+ 11·1
KIO_3 = KI + O_3 absorbs	− 44·1

Not only is the decomposition of the iodate more difficult owing to its endothermal character, but it is accompanied by phenomena of dissociation, the dry potassium iodide absorbing the free oxygen.[1] Chloric (− 12·0), bromic (− 24·8), and iodic

[1] "Annales de Physique et de Chimie," 5ᵉ série, tom. xii. p. 313.

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(+ 22·6), acids diverge still more, one from the other, and present differences which are not the same as for their salts.

9. Let us now compare the three principal reactions to which the systems formed by halogens and alkali are susceptible.

(*a*)

$3Cl_2$ gas + $3K_2O$ (diluted) = 3KClO (dissolved) + 3KCl (dissolved) + 76·2
$KClO_3$ (dissolved) + 5KCl (dissolved) ... ... + 94·2
6KCl (dissolved) + O_3 ... ... + 111·0

The liberation of heat and the stability continue to increase from the hypochlorite to the chlorate and free oxygen.

(*b*)

$3Br_2$ (gas) + $3K_2O$ (dissolved) = 3KBrO (dissolved) + 3KBr (dissolved) + 57·6
$KBrO_3$ (dissolved) + 5KBr (dissolved) ... ... + 54·0
6KBr (dissolved) + O_3 ... ... + 74·4

The formation of hyprobromite liberates a rather greater quantity of heat than that of the bromate, which explains the relative stability of the former compound. However, the formation of bromide and oxygen is still the reaction which liberates most heat. It is, moreover, well known that concentrated potash can yield oxygen by its action on free bromine.

(*c*)

$3I_2$ + $3K_2O$ = 3KIO (dissolved) + 3KI (dissolved) ... + 24·9 − 3a
KIO_3 (dissolved) + 5KI (dissolved) [1] ... ... + 31·8
6KI (dissolved) + O_3 ... ... − 12·3

Here the formation of the iodate exceeds all the others. The liberation of oxygen would even involve an absorption of heat, contrary to what takes place with the chlorate and bromate. Moreover, this liberation does not take place at the ordinary temperature; it is only effected with the aid of a foreign energy which is got in the act of heating.

We see that the principal chemical circumstances attending the formation of the combinations between oxygen and the halogens are in harmony with thermal data.

[1] Calculated from the figures on p. 360, admitting that they represent a maximum value for the formation of hypoiodite.

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CHAPTER XIII.

METALLIC OXALATES.

1. THERE exists a certain number of non-nitrogenised compounds, formed in a regular manner, *i.e.* from the elements, in consequence of a succession of exothermal reactions, which, nevertheless, through heating or a shock capable of determining decomposition, give rise to explosive phenomena. They are compounds of such a kind that their elements have not reached the most stable state of combination, *i.e.* the state to attain which they have liberated the greatest possible amount of heat.

We have, for instance, silver and mercuric oxalates—bodies which detonate when suddenly heated or submitted to a violent shock. Such a decomposition converts them into carbonic acid and metal, in consequence of a real *internal combustion* by which the oxygen of the metallic oxide attacks the oxalic acid and completely oxidises it. This combustion, however, is only possible when the heat it liberates surpasses that of the oxidation of the metal plus the heat of neutralisation of the metal. In other words, in order that an oxalate may possess such properties, the reaction

$$M_2C_2O_4 = 2CO_2 + M_2$$

must be exothermal. Such is the fundamental condition which distinguishes explosive oxalates from such as are not.

2. Let us elucidate these notions by calculating the heat brought into play by the decomposition of the principal metallic oxalates.

For this purpose the heat of formation of dissolved oxalic acid from its elements[1] was first measured—

$$H_2 + C_2 \text{ (diamond)} + O_4 \text{ water} = H_2C_2O_4 \text{ (dissolved) (90 grms.)} \text{ liberates } + 194{\cdot}7 \text{ Cal.}$$

[1] "Annales de Chimie et de Physique," 5e série, tom. vi. p. 304.

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We find, moreover, the heat of formation of metallic oxides in the tables (p. 130).

These are the values relative to the more common metallic oxalates:—

$Zn + O = ZnO$	...	...	...	+ 86·4
$Pb + O = PbO$	...	—	...	+ 53·4
$Cu + O = CuO$	...	...	...	+ 38·0
$Hg + O = HgO$	...	...	...	+ 31·0
$Ag_2 + O = Ag_2O$	...	...	...	+ 7·0

By the method of double decomposition the heat liberated by the union of the metallic oxides with oxalic acid was measured; or [1]

$H_2C_2O_4$ (diluted) + ZnO (precipitated)	= $ZnC_2O_4 + H_2O$	...	+ 25·0
$H_2C_2O_4$ „ + PbO „	= $PbC_2O_4 + H_2O$	...	+ 25·6
$H_2C_2O_4$ „ + CuO „	= $CuC_2O_4 + H_2O$	...	+ 18·4
$H_2C_2O_4$ „ + HgO „	= $HgC_2O_4 + H_2O$	...	+ 14·0
$H_2C_2O_4$ „ + Ag_2O „	= $Ag_2C_2O_4 + H_2O$	...	+ 25·8

These data having been obtained, it is only necessary to add together the heats of formation of the oxalic acid, the metallic oxide and that of their reciprocal combination, and then deduct the heat of formation of water, H_2O (69 Cal.), in order to find the heat of formation of the metallic oxalate from its elements.

Acid (solid)	...	$H_2 + C_2 + O_4 = H_2C_2O_4$	...	+ 197·0
Zinc salt	...	$Zn + C_2 + O_4 = ZnC_2O_4$	...	+ 237·1
Lead salt	...	$Pb + C_2 + O_4 = PbC_2O_4$	...	+ 204·7
Copper salt	...	$Cu + C_2 + O_4 = CuC_2O_4$	...	+ 182·1
Mercuric salt	...	$Hg + C_2 + O_4 = HgC_2O_4$	...	+ 170·7
Silver salt	...	$Ag_2 + C_2 + O_4 = Ag_2C_2O_4$	...	+ 158·5

3. If we note the heat of formation of 2 eq. of carbonic acid from carbon (diamond) and oxygen, or

$$2(C + O_2) = 2CO_2 \text{ liberates } + 188{\cdot}0,$$

it is easy to calculate the heat brought into play when an oxalate is decomposed into gaseous carbonic acid and free metal, the reaction being referred to the ordinary temperature—

$H_2C_2O_4$ (solid) = $H_2 + 2CO_2$	...	...	− 9·0
ZnC_2O_4 = Zn (solid) + $2CO_2$	...	...	− 49·1
PbC_2O_4 = Pb (solid) + $2CO_2$	...	...	− 16·7
CuC_2O_4 = Cu (solid) + $2CO_2$	..	...	+ 5·9
HgC_2O_4 = Hg (liquid) + $2CO_2$	...	...	+ 17·3
$Ag_2C_2O_4$ = Ag_2 (solid) + $2CO_2$	...	...	+ 29·5

4. We see from this that zinc and lead oxalates cannot be decomposed into carbonic acid and metal with a liberation of

[1] The calculation is made here on the supposition that the precipitated oxalates are anhydrous, or rather, that the heat liberated is essentially the same for the anhydrous and precipitated salts; which, in fact, has been proved to be the case for the salts of mercury and silver.

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heat. In fact, this reaction does not take place; at least, not without a strange complication.

It would seem at first sight that oxalic acid is in the same position; but this is only true when we start from the acid in a solid state. In fact, the acid partly assumes the gaseous state, at the moment of decomposition; for observation proves that a portion is always volatilised under these conditions. However, this volatilisation of the solid acid must from analogy absorb about 8 to 12 Cal. Taking this quantity into consideration, we see that oxalic acid, when gaseous, is on the confines of an exothermal decomposition, which explains its instability. When the acid is in solution, the decomposition is in reality exothermal, for

$$H_2 + C_2 + O_4 + \text{water} = H_2C_2O_4 \text{ liberates} + 194{\cdot}7,$$

while

$$2CO_2 \text{ (gas)} + \text{water} = 2CO_2 \text{ (dissolved)} + 199{\cdot}2.$$

The difference, + 4·5 Cal., represents the heat liberated in the reaction. Copper oxalate is also on the confines, and even beyond, its decomposition being exothermal. Finally, that of mercuric and silver oxalates is positively exothermal.

5. Nevertheless, as regards mercuric oxalates the heat liberated is limited, from a certain temperature, by the volatilisation of the mercury, which absorbs − 15·4; but this restriction does not exist in the case of silver oxalate; and, in fact, this compound is very explosive. It explodes very energetically when subjected to a shock or when heated to about 130°. At 100° and lower it decomposes slowly and progressively.

We see from these facts how thermo-chemistry explains the explosive properties of certain metallic oxalates, and also the difference which exists between the conditions of decomposition of these and other oxalates.

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BOOK III.

FORCE OF EXPLOSIVE SUBSTANCES IN PARTICULAR.

CHAPTER I.

CLASSIFICATION OF EXPLOSIVES.

§ 1. DEFINITION OF EXPLOSIVES.

1. ANY system of bodies capable of developing permanent gases or substances which assume the gaseous state in the conditions of reaction, such as water above 100°, mercury above 360°, etc., may constitute an explosive agent. Even gaseous bodies assume the same character if compressed beforehand, or if their volume increases in consequence of some transformation. For this purpose it is not necessary that the temperature of the system should rise, although this condition is generally fulfilled and tends to increase the effects.

2. Nevertheless, this definition of explosive agents, although exact from an abstract point of view, is too wide for practice, which only utilises such systems as are susceptible of a rapid transformation and accompanied by the liberation of great heat.

3. Moreover, the initial system should be able to subsist of itself, at least for some time; its transformation only taking place if provoked by some external circumstance, such as fire, shock, friction, or again by the intervention of small quantities of a chemical agent, acting either in consequence of its own reactions, which propagate themselves chemically (sulphuric acid in presence of potassium chlorate mixed with organic substances), or because it produces a sudden shock, determining by its mechanical effects the production of the explosive wave (p. 88) and general explosion.

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§ 2. General List of Explosives.

1. Let us enumerate the explosive bodies which fulfil these conditions. They belong to eight distinct groups of substances. These are—

First group.—*Explosive gases*, such as—

(1) Ozone, hypochlorous acid, the gaseous oxides of chlorine, etc., which detonate under very slight influences—for instance, slight heating or sudden compression.

(2) Various *gases also formed with absorption of heat*, but more stable, gases which do not explode under the influence of progressive heating or moderate compression. Nevertheless, they may explode through the detonation of mercury fulminate. Such are acetylene, nitric oxide, cyanogen, arseniuretted hydrogen, etc. (p. 66).

2. Second group.—*Detonating gaseous mixtures* formed by the association of oxygen or chlorine, oxides of nitrogen with hydrogen, hydrogenated gases, and carburetted and hydrocarburetted gases or vapours.

3. Third group.—*Explosive inorganic compounds, definite bodies, liquids or solids*, capable of exploding by shock, friction, or heating, such as—

(1) Nitrogen sulphide, nitrogen chloride, and nitrogen iodide. Mercury nitride and some other metallic nitrides. Fulminating gold and mercury oxides, which are also nitrated derivatives.

(2) The liquid oxacids of chlorine and concentrated permanganic acid.

(3) Solid ammoniacal salts formed by the oxacids of chlorine, nitrogen, chromium, manganese, and similar substances.

4. Fourth group.—*Explosive organic compounds, definite bodies, solid or liquid*, capable of exploding by shock, friction, or heating, such as—

(1) Nitric ethers properly so called; nitric ether, nitroglycerin, nitromannite, etc.

(2) The nitric derivatives of the carbohydrates: cotton, paper, wood, various kinds of cellulose, dextrine, sugar, etc.

(3) Nitro-derivatives, especially aromatic derivatives—for instance, trinitro-phenol and its salts (picric acid and picrates), nitro-oxyphenol (oxypicric acid and oxypicrates), tetranitromethane, chloropicrine (chloronitro-methane). Nitromethane and its homologues, as well as their derivatives, are also classed here.

(4) The diazo derivatives, such as diazobenzene nitrate and similar bodies, nitrolic acids and other polynitro-derivatives, nitro ethane, to which the fulminates of mercury and silver, etc., seem to belong.

(5) The derivatives of highly oxygenated mineral acids, such as, on the one hand, nitrites, nitrates, chlorates, perchlorates,

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chromates, permanganates of organic alkalis; on the other hand, nitrous ethers, perchloric ethers, etc.

(6) Here we may also add the explosive derivatives of hydrogen peroxide; ethyl, acetyl, etc., peroxides.

(7) The hydrocarbon derivatives of mineral oxides which can be easily reduced, especially the salts of silver and mercury oxides, such as silver oxalate, mercury oxycyanide, etc.

(8) The derivatives of the hydrocarbons and other bodies characterised by an excess of energy with relation to their elements, such as metallic acetylides, etc.

5. Fifth group.—*Mixtures of definite explosive compounds with inert bodies.* Each of the preceding compounds, whether solid or liquid, can be mixed with inert bodies, destined to attenuate the effects. Dynamite, properly so called, with a silica or alumina base, wet gun-cotton, or soaked with paraffin, nitroglycerin dissolved in methylic alcohol, camphorated gun-cotton and dynamite, etc., constitute such mixtures.

6. Sixth group.—*Mixtures formed by an explosive oxidisable compound and a non-explosive oxidising body destined to complete the combustion of the former.* Such are—

(1) Gun-cotton mixed with potassium or ammonium nitrate potassium picrate mixed with potassium chlorate or nitrate, etc

(2) Also the mixtures of nitric acid with nitro compounds, such as dinitrobenzene, the nitrotoluenes, picric acid (trinitrophenol), etc., generally mixed in the form of paste.

(3) The mixtures of nitric peroxide and nitro compounds are also classed here.

7. Seventh group.—*Mixtures with an explosive oxidising base.*

(1) The mixtures formed by an explosive body containing an excess of oxygen (nitroglycerin, nitromannite) and an oxidisable body such as carbon dynamite.

(2) Analogous bodies, in which the oxidising and oxidisable bodies are both explosive, such as blasting gelatin formed by the association of nitrocellulose and nitroglycerin, etc.

8. Eighth group.—*Mixtures formed by oxidisable and oxidising bodies, solid or liquid, neither of these being explosive separately.* This group comprises—

(1) Black powder formed by the association of sulphur and carbon with potassium nitrate and constituting the varieties designated as service, sporting, and blasting powder, etc.

(2) The various powders formed by the association of hydrocarbon compounds, charcoal, coal, wood, sawdust, various kinds of cellulose, starch, sugar, ferrocyanide, or by the association of sulphur and metals with potassium, sodium, barium, strontium, lead, etc., nitrates.

(3) The liquid or pasty mixtures formed by the association of liquid nitric acid either with a combustible liquid or with a solid substance on which it does not exercise an instantaneous action.

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(4) Here we may class the mixture of liquid nitric peroxide with various oxidisable substances, such as carbon disulphide or petroleum spirit.

(5) The powders formed by the association of combustible bodies with chlorates and perchlorates.

(6) The powders formed by the association of combustible bodies with various combustive bodies, such as potassium bichromate, chromic acid, the oxides of copper, lead, antimony, bismuth, etc.

(7) To the mixtures of this group may be assimilated the mixtures formed by the association of a sulphide, a metallic phosphide or an analogous binary compounds with another metal capable of displacing the former under the gaseous form (mercury, for instance) with the liberation of heat.

§ 3. Division of the Third Book.

The variety of explosive mixtures thus practically created with a view to their being applied is indefinite. Nevertheless the number of the usual compounds is limited, and we will designate the principal ones we intend to examine specially; but first of all, in Chapter II. we shall present the general data which it is necessary or useful to know in order to define the manufacture and employment of a given explosive.

Chapter III. will comprise the study of explosive gases, detonating gaseous mixtures, and analogous substances (groups 1 and 2).

Chapter IV. is devoted to non-carbonated explosive compounds (3rd group).

In Chapter V. we shall treat of nitric ethers properly so called (4th group).

The sequence of the substances belonging to this group is studied in the following four chapters, which also comprise the mixtures of the 5th, 6th, and 7th groups. The dynamites will be examined in Chapter VI.

Gun-cotton and allied bodies in Chapter VII.

Picrates in Chapter VIII.

Dinitro compounds in Chapter IX.

Lastly the eighth group will be examined, viz.: Powders with a nitrate base in Chapter X.;

Powders with a chlorate base in Chapter XI.

And we shall conclude with some general considerations.

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CHAPTER II.

GENERAL DATA RESPECTING THE EMPLOYMENT OF A GIVEN EXPLOSIVE.

§ 1. THEORETICAL DATA.

1. EXPLOSIVE bodies cannot be employed profitably and securely unless they are characterised by a certain number of data, theoretical as well as practical, which will now be enumerated.

2. First as regards theoretical data. They have been given in principle in Book I.; but it seems desirable to summarise them here from a more special point of view. These data refer to eight orders of measurements, namely:

(1) The chemical equation of transformation.

(2) The heats of formation of the components and products.

(3) Their specific heats.

(4) Their densities.

(5) The pressures developed.

(6) The initial work which determines the reaction (temperature of inflammation, nature of shock, etc.)

(7) The law which determines the rapidity of the transformation with reference to temperature and pressure.

(8) The total work which an explosive substance can effect (potential energy).

Each of these orders of measurements embraces several distinct determinations.

3. The chemical equation of the explosive transformation comprises:

(1) A knowledge of the *original bodies* and of the *products* as regards their nature and relative weight.

(2) The knowledge of the *volume of the permanent gases*, reduced to 0° and 0·760 metres, which the transformation develops (p. 18). This volume may be calculated *à priori*, or measured directly and as an essential element of chemical analysis.

(3) A knowledge of the *gaseous volume* (reduced by calculation to 0° and 0·760 metres) of the products actually liquid or solid,

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but capable of assuming the gaseous state at the temperature of explosion. Much discussion often arises on this head.

(4) The knowledge of the *state of dissociation* of the products at the moment of explosion and during the period of cooling (p. 8).

In fact, up to the present this datum is known with precision for scarcely any compound body, and our ignorance in this respect is one of the principal causes of the divergence observed between the practical results and the data of theoretical calculation.

(5) The knowledge of the *weight of oxygen actually employed* in the explosive reaction.

(6) The knowledge of the *weight of oxygen required* for total combustion is deduced from the preceding.

4. The heats of formation of the components and products comprise:

(1) The knowledge of the heats of formation of these various bodies from their elements; quantities given in the thermochemical tables (p. 125 and following).

(2) *Their heat of total combustion by free oxygen*, or *by the oxidising compounds* (nitrates, chlorates, oxides, etc.).

(3) The knowledge of the heat of vaporisation of bodies actually *liquid* or *solid*, but capable of assuming the gaseous state in the conditions of the explosion (p. 140).

(4) *The heat liberated by the explosive transformation* is also deduced from the foregoing data, which are supposed to be known. On the other hand, it may be measured directly and employed in the inverse calculation of these same data.

5. The specific heats of the components and products are generally known by the tables for the ordinary temperature (pp. 141–143). For high temperatures, such as are developed during the explosion, our knowledge on this point is very imperfect.

From the mean specific heat of the products is deduced the temperature developed during the explosion. The calculation is made according to the knowledge of the quantities of heat (pp. 11 and 19); but the accuracy of the result is subordinated to the knowledge of the dissociation and that of the specific heats (see p. 18).

Processes of direct measurement for the temperatures would be preferable; but hitherto it has not been possible to try them with any probability, except in one single case, namely with black powder.

6. The densities of the components and products may be measured at the ordinary temperature (p. 144).

(1) The molecular volumes are obtained from them. A knowledge should be added of the co-efficients of expansion of the various solid, liquid, or gaseous bodies, so as to deduce

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therefrom the exact volume of the products at the temperature of explosion. Unfortunately these are data which are but little known, and we generally content ourselves with the densities in the cold for solids and liquids, and the densities calculated according to Mariotte's and Gay-Lussac's laws for gases.

(2) These data are necessary to calculate *à priori*, according to the same laws, the *theoretical pressure* which the explosive would develop when detonating *in its own volume* (p. 30).

(3) They would be equally useful for calculating *the theoretical pressure under any density of charge* (p. 30), that is to say, the real volume occupied by the gases at the moment of explosion; but for this purpose the real density of solid, liquid, and gaseous products should be known exactly.

7. The pressures developed must be measured directly (p. 20).

(1) Under various densities of charge.

(2) A *curve* is deduced therefrom which permits us to estimate *according to the experiments themselves*, the real pressure developed under a density equal to the unit, viz. the *specific* pressure (p. 30) as well as,

(3) The *maximum pressure* developed by the explosive. It is that of a body detonating in its own volume (p. 30).

If we admit that there exists a proportion between the pressures and high densities of charge (p. 30), the specific pressure, namely the pressure developed under a density, equal to the unit, will characterise the force of the explosive.

The effective measurements thus obtained for the *real pressures* should be compared with the *theoretical pressures* calculated, as has been said, with the aid of Mariotte's and Gay-Lussac's laws. In this calculation the volume occupied by the solid or liquid products must be taken into account.

(4) A more certain datum, and one that is more easily calculated *à priori* and verified experimentally, is the permanent pressure exercised by the gases of explosion reduced to 0° in a determinate and sufficiently resisting capacity (p. 32). It is often limited by the liquefaction of the products, such as carbonic acid.

(5) As a term of comparison, the *characteristic product*, if not absolute at least relative, can be given, namely, the product of the heat liberated multiplied by the reduced volume of the gases and divided by the specific heat of the bodies formed (p. 32). This product gives essentially in theory the same relations between the various explosive substances as the theoretical pressure.

8. The initial work which determines the reaction seems to be summed up in a knowledge of the following data:—

(1) The *temperature of incipient reaction*, a temperature which must be measured directly.

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(2) The smallest shock which will cause decomposition, also the effects due to the shock, or the application of fire would be, no doubt, derived therefrom in a complete theory.

In the absence of this theoretical datum, we measure the minimum fall of a given weight which is required to cause the substance to explode when placed in definite conditions.

More generally, but in a vaguer manner, we ascertain whether it explodes by the shock of iron on iron, bronze on bronze, stone on stone, wood on wood, iron on bronze, stone, wood, bronze on stone or wood, stone on wood, or by friction exercised in various conditions, etc.

9. The law of the rapidity of decomposition, in cases of simple ignition, and the rapidity of propagation of the explosive wave in other cases (p. 88), is of primary importance, but this law is generally not known.

10. The total work performed by an explosive substance in given conditions corresponds to the difference between the heat liberated by the chemical transformation effected without external work and the heat really liberated in the conditions of the experiment, a difference which might, if necessary, be measured experimentally.

In principle the maximum work would be measured by the liberated heat itself (potential energy), but we have only to consider the work which may be performed by the gases developed by the explosion in the case of indefinite expansion. The theory of these effects has only been broached for service powder (p. 17).

11. In practice this deficiency is made up by empirical notions drawn from the study of the effects of each explosive on various kinds of vessels and materials. These effects are moreover complex, for they often result at the same time from the total work, the pressure exercised, the law of rapidity, and the nature of the materials.

Without entering into circumstantial details, may be cited as an instance the trial of the force of an explosive substance according to the size of the capacity produced by its explosion in a block of lead (Abel's process). For instance, a block of lead is taken, 250 mm. square, 280 mm. high, and weighing 175 kgm. Following the axis, a cylindrical channel is bored with a diameter comparable to that of a miner's boring tool (28·5 mm.), and 178 mm. deep. A determinate weight of the explosive substance (10, 20, or 30 grms.) is placed at the bottom, and if necessary it can be arranged under an impermeable covering. A detonator is introduced at the end of a fuse of suitable length, and the hole is then filled up with water, which serves as tamping. The explosion is then effected, and the capacity of the pear-shaped chamber produced is afterwards measured. The proportion between the increase of the capacities

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produced under the influence of equal weights of the various explosives may be taken as comparative measurements of their power. When the substance is too active, a system of rents is produced, following almost a diagonal direction in any vertical section passing through the axis of the block, and tending to detach a kind of truncated cone in the total mass. This accident can, however, be avoided by diminishing the weight of the substance.

It has been found that the relations of the increases of capacity obtained with variable weights of different materials remain the same, the weight being moreover very small in comparison with that of the block. Here are some of these relations which express the increase of capacity produced by 1 grm. of explosive according to the experiments of the Commission des substances explosives :—

	cc.
Nitromannite	43
Nitroglycerin	35
Dynamite 75%	29
Dry gun-cotton	34
Ditto (0·40 grm.) + ammonium nitrate (0·60 grm.)	32
Ditto (0·50 grm.) + potassium nitrate (0·50 grm.)	21
Mercury fulminate	13·5
Ditto, eliminating the weight of the mercury by calculation ...	45
Panclastites: 1 vol. carbon disulphide + 1 vol, nitric peroxide	25
2 vols. CS_2 + 1 vol. NO_2	18
3 vols. CS_2 + 5 vols. NO_2 (complete oxidation)	28
1 vol. essence of petroleum [1] + 1 vol. NO_2	28
2 vols. essence of petroleum [1] + 1 vol. NO_2	18
1 vol. nitrotoluene + 1 vol, NO_2	29

This process furnishes very interesting comparative data, but it does not apply to slow powders, such as black powder, as the tamping is then driven forward before the chamber has been enlarged.

In the case of rapid powders the relations are not the same as those resulting from the quantities of heat and of the gaseous volumes. Thus these two quantities are nearly the same for nitroglycerin and nitromannite, whereas the capacities are greater by a fourth in the case of the latter substance, doubtless because its explosion is effected in a shorter time.

The classification of the relative force of explosives according to their effects changes very much according as the operation is carried out with or without tamping. Generally speaking, studies of this kind are only fully valid for works, effects, and materials comparable to those which formed the object of the preliminary experiments.

12. Such is the ensemble of the scientific data we must endeavour to obtain before laying claim to the complete theory of a given explosive substance.

[1] Containing one-tenth of its volume of carbon disulphide.

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In fact and in practice these data are less numerous than might be inferred from the preceding statements. In the present state of our knowledge they are reduced practically to the following:—

(1) Chemical equation of the transformation.

(2) Heat developed by this transformation.

(3) Volume reduced to 0° and 760 mm. of the gases and bodies capable of being rendered gaseous in the conditions of the transformation.

(4) Pressures developed.

(5) More or less crude empirical indications referring to the work effected.

These five orders of data regulate our knowledge of the force of explosive substances.

Let us remark here that the first three measurements are deduced simply from the chemical equation of the phenomenon, and the thermo-chemical tables; the fourth and fifth would be calculated by the preceding if the laws respecting the thermodynamics of gases and those of the resistance of substances were sufficiently well known.

§ 2. Practical Questions respecting the Employment of Explosive Substances.

1. In practice an explosive substance must satisfy a certain number of conditions which we will now summarise. These conditions refer to the employment, manufacture, preservation, and stability of the explosive substance. Let us commence with the employment.

2. The explosive substance placed in a *small volume* and under a moderate weight should develop a *considerable quantity of gas* and a *great amount of heat*, circumstances which exclude explosive gases and detonating gaseous mixtures, at least in most applications.

3. The *chemical transformation* which the substance undergoes should be *produced in a very short space of time*, so that the heat may not be gradually dissipated, which would greatly reduce the pressure.

Let us remark, moreover, that the effort of a sudden pressure produces very different effects of rupture on a given substance to what would have been the case if the same pressure had been exercised slowly.

In mining works, or with firearms, a slow reaction would tend to let the gases escape little by little through the interstices of the earth or the charge.

4. *The empirical measurement* of the force of an explosive substance will be effected by means of a system of tests approaching as far as possible the conditions of its practical employment.

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In the absence of these conditions, which are not very suitable for precise comparisons, trials are made on a small scale, such as—

The use of the testing mortar on ballistic pendulum for powders intended to throw projectiles from firearms;

The use of bombs of different thicknesses from which the bursting charge (p. 58) and the mode of fragmentation are studied;

The rupture of freestone, rails, T-iron, iron girders, masses of rolled, cast, or wrought iron, beams of different kinds of wood, and different scantlings, by charges laid on their surface;

The curve imparted to thick iron plates in comparative conditions;

The crushing of a small block of lead by a charge placed on its surface, with or without tamping;

The crushing of a copper cylinder (p. 20);

The form and size of the chambers produced in a mass of clay or lead by the explosion of an internal charge (see p. 374), etc.

We shall refer to the technical treatises and memoirs for the description of these various tests, as it would be almost impossible to give the exact theory of them at present.

5. The explosive substance should be capable of being handled and transported by road or railway with at least relative safety, and it must not be too sensitive to shocks or friction. This is the reason why pure nitroglycerin and chlorate powders are almost excluded in practice.

The same circumstance forbids the employment of dynamite and pure gun-cotton in warfare, since these substances explode from the shock of a ball.

6. The substance should only explode in conditions which are precisely known, and capable of being produced or avoided at pleasure; for instance—special ignition, the use of certain caps and fuses; the employment of electricity to heat a wire or produce a spark; the shock of two metal pieces arranged beforehand; definite chemical reaction—for instance, that of sulphuric acid on potassium chlorate mixed with a combustible body, etc.

The conditions under which the explosive substance is brought to explode should be realisable without too much difficulty; thus the explosion of paraffined gun-cotton becomes almost impossible above a certain quantity of paraffin. In the same way a mixture of petroleum spirit and nitric peroxide in equal volumes does not explode under the influence of an ordinary fulminate cap, while it does so by the addition of a tenth part of carbon disulphide, etc.

7. The explosion should produce effects foreseen beforehand, at least in a certain limit, such as direction, general characters, and intensity.

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Thus too sudden a reaction brought about in a firearm causes its rupture before the projectile has time to be displaced. Any substance capable of producing such effects must be excluded, and this prevents the employment of pure nitroglycerin or potassium picrate in firearms.

A shell should be broken into large pieces and not pulverised by the explosion of the internal substance, and this circumstance opposes the use of pure mercury fulminate. The reaction of the powder in the weapon should be sufficiently progressive for the projectile to acquire a determinate initial velocity.

8. From a more particular point of view, the explosive substance should *not injure the weapons;* either by chemical reaction, sulphurising, oxidation, etc., or by fouling (ash and fixed substances, leading, etc.), or by mechanical wear and tear.

9. In subterranean works the explosive substance must not produce any *deleterious gases* capable of suffocating the workmen (carbonic oxide, sulphuretted hydrogen, nitrous vapours, hydrocyanic vapours, etc,).

In general it should not produce *too much smoke* in warfare.

10. On the contrary, *in certain military operations* it may be *useful to produce a great deal of smoke,* in order, for instance, to mask a movement or some works.

It may also be useful to *produce deleterious gases* in order to render the gallery of a mine, etc., impracticable for some time.

11. The pyrotechnical effects, such as signals, lighting, bonfires, etc., represent quite a different order of special conditions to be fulfilled, but on which we shall not dwell, as this subject is foreign to the present work.

12. The *necessity of dividing the explosive substances,* or of making them into a determinable form, enters into consideration sometimes.

Thus dynamite and the powders properly so called are more easily divided than gun-cotton into small pulverulent masses, destined to be introduced into some cavity whose cracks and fissures they fill up, such as a blast-hole.

On the other hand, compressed gun-cotton may be easily divided and worked with tools so as to give it a special form independent of any covering; special care is taken to impregnate it beforehand with paraffin, a substance which moreover has the advantage of diminishing the explosive sensitiveness of gun-cotton.

13. In various cases the explosive substances *are compressed* or agglomerated under an hydraulic press in order to increase the density and modify the law of propagation of the ignition. Black powder and gun-cotton are very suitable for this operation, which it would be perilous to attempt with fulminate or chlorate powders.

14. Let us cite again the employment of fulminating substances under the form of *caps, ordinary or strong detonators,*

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which are destined to provoke the explosion of a considerable mass of another substance (p. 54).

They are treated in small quantities, and precautions are taken against the dangers presented by their preparation and manipulation, dangers which would not be accepted in industries for a substance manufactured or employed in large masses.

We shall restrict ourselves to the indications which have just been enumerated and which correspond to the principal uses of explosive substances in war and industry. As regards the effects themselves which it is proposed to accomplish, it can easily be understood that the diversity of these special effects required from explosive substances is unlimited.

§ 3. Practical Questions referring to the Manufacture.

1. The manufacture of explosives ought to be effected under conditions of cost proportioned to their industrial uses, one and the same effect being produced in mines or industries in general at the lowest possible price. In military matters this condition also intervenes, but in a minor degree, since facility and safety of employment outweigh all other considerations.

2. The *manufacture* must be *carried on regularly* and *without danger*, or at least with as little danger as possible to the work-people and neighbourhood.

3. The inconveniences resulting through *noxious gases, noise,* and damage arising from accidental explosions must also be taken into consideration.

§ 4. Practical Questions respecting Preservation.

1. It should be possible to *keep explosives without any spontaneous decomposition* in the ordinary state of the atmosphere, in various climates, under moderate conditions of temperature and light, in an average hygrometric state, etc.

2. Direct sunlight is bad for nitro compounds, as it often leads to their chemical decomposition.

3. *Extensive variations* of *temperature* also exercise an important influence, particularly if they determine the freezing of certain ingredients, such as nitroglycerin in the dynamites, or if they increase the fluidity of certain bodies, such as nitroglycerin itself, and consequently their tendency to exudation. The separation between nitroglycerin and its absorbent can thus take place by the fact of repeated variations of temperature or even of repeated freezing and thawing. Under the influence of a somewhat high temperature, such as occurs in practice, especially in hot countries, certain compounds may gradually evaporate slowly and modify the primitive composition of the mixtures. This occurs, for instance, to ordinary dynamite heated

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for a long time on a sand-bath, as the nitroglycerin gradually evaporates and the substance consequently loses part of its power.

The elevation of the temperature might also give rise to the *rapid vaporisation* of certain components and consequently to their elimination, for instance in the case of compounds containing nitric peroxide, which boils at 26°.

4. The state of preservation should remain satisfactory even in very *varied hygrometric conditions* of the surrounding atmosphere.

It is this condition which has led to deliquescent bodies such as sodium nitrate being excluded from the manufacture of service powder. This salt should also be avoided in the manufacture of dynamite, seeing that the accidental formation of a concentrated solution of sodium nitrate due to the deliquescence of the solid salt determines the separation of the existing nitroglycerin and transforms this substance into a non-homogeneous and very dangerous mixture.

Diazobenzene nitrate becomes completely decomposed under the influence of moisture.

5. The salts with which *sea air* is impregnated constitute a special cause of change which must be borne in mind, especially as regards explosives which are to be employed on board ships, or even conveyed by them, since the air eventually penetrates into the best closed vessel, owing to the variations of temperature and pressure.

6. From this point of view it is useful to know whether an explosive substance resists the *action of liquid water*, which may accidentally moisten explosive substances, especially at sea. It is well known that water destroys service powder by dissolving the saltpetre: by a kind of liquefaction it gradually displaces the nitroglycerin in silicious dynamite.

Dynamites which contain nitrates are also decomposed by water.

Silicious dynamite deposited in running water gradually loses its nitroglycerin by way of solution, since nitroglycerin is slightly soluble in water.

On the other hand, pure water does not affect gun-cotton whether the latter be simply moistened or plunged into running water. The inflammability of the substance, which is checked by the presence of water, reappears completely after drying.

Moistened gun-cotton can moreover be kept and even employed in that state with less danger of accidental ignition than in the dry state.

However, gun-cotton which is kept moistened for a long time may become the seat of mould and other microscopic plants which alter the properties in the long run.

7. The slow exudation of the nitroglycerin in dynamites made with bad materials forms an obstacle to their preservation,

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and also a serious danger, for it tends to substitute pure nitroglycerin for a substance which is but little sensitive to shocks or friction, while the former is, on the contrary, extremely sensitive.

It has been stated how freezing followed by thawing, and even the action of water, might also give rise to exudation.

8. The possible separation of the various ingredients of a mixture under the influence of jolting arising from conveyance by sea or land is also to be considered.

9. The *slow action which the metals*, constituting metallic cartridges, exercise on the saltpetre and the sulphur contained in cartridges, especially if these are even slightly hygrometric, may determine the oxidation and sulphurising of these metals at the expense of the saltpetre and sulphur. Hence there arises at length a certain weakening of the effects obtained with recent powders, according to the experiments made by Colonel Pothier.

We then see how the preservation of explosives gives rise to very varied special problems. It suffices at present to have pointed out the preceding.

§ 5. Tests of Stability.

1. The tests of stability to which a given explosive is subjected in practice, comprise the most essential conditions among those which have been just enumerated. These are—

2. *Stability on exposure to air.* The substance must maintain itself, when in contact with air, without evaporation, liquefaction, or apparent alteration, even after having been kept several days. It must not attract atmospheric moisture.

3. *Neutrality.* It should in general be neutral and preserve this neutrality; above all, it must not liberate acid vapours even when heated for some minutes in a bath kept about 60°.

4. *Exudation.* It must not allow the liquid substances it contains, such as nitroglycerin, to exude, either spontaneously or by a slight pressure such as is applied when pushing back the substance gently with a wooden piston in a brass tube pierced with lateral holes. In this trial the piston should not be pressed by hand but by a weight, which is gradually increased until exudation takes place.

When heated to about 55° to 60° in a bath, the substance should not give rise to the separation of small drops even under a slight pressure.

When subjected to a temperature below zero, and then brought back to the ordinary temperature, and that several times, it ought also not to produce exudation.

Nor should exudation take place under the influence of air saturated with moisture; for instance, should the substance be left for a fortnight in a chamber containing damp tow.

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It should also be ascertained whether the substance, when subjected for several days to a series of shocks in conditions similar to such as would arise during conveyance by sea or land, occasions the separation of some of its components.

These exudation tests are, above all, essential as regards dynamites, as the separation of the nitroglycerin tends to make them very dangerous.

5. *Shock.* It should be tried whether the substance explodes by the shock of a hammer on an anvil, or better still by the fall of a given weight falling from various heights on a portion of the substance placed on an anvil.

An explosive should not explode through the shock or friction of wood on wood or of wood on metal (bronze or iron). Some substances do not explode by the shock of bronze on bronze, but do so by iron on iron.

The accidental introduction of some grain or fragment of sand or other hard rock facilitates the explosion, especially by friction.

The action of the shock of bullets at different distances should be studied, especially in the case of substances intended for military operations.

6. *Immersion.* The explosive substance is placed under water without any covering for fifteen to twenty minutes. It ought neither to dissolve nor split up, nor give rise to the separation of small liquid drops. This test is only applicable to substances which are liable to be in contact with water when used.

7. *Heat.* It is first ascertained whether the substance becomes inflamed when in contact with an ignited body, and how it burns in this condition.

The influence of very slow progressive heating is also studied in order to see whether it gives rise to the partial evaporation of any of its components.

We then proceed to more rapid heating, placing, for instance, a small quantity of the substance in a thin metallic capsule, which is laid on the surface of an oil or a mercury bath[1] maintained beforehand at a fixed temperature. It is ascertained at what temperature the explosion takes place, and whether simple burning or even progressive decomposition can take place at a lower temperature.

These general questions being defined, we proceed to the study of the various groups and kinds of explosive substances. Let it, however, be remembered that it is not intended to give an individual and a practical history of each of them in all its details, which would lead us too far; but we especially wish to point out the scientific data which characterise them by studying the principal explosive bodies hitherto known, these bodies being considered as typical of all similar substances.

[1] The capsule must then be made of platinum.

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CHAPTER III.

EXPLOSIVE GASES AND DETONATING GASEOUS MIXTURES.

§ 1. Division of the Chapter.

This chapter comprises the study of definite explosive gases; of detonating gaseous mixtures formed, for instance, by the association of oxygen with a combustible gas; of liquefied mixtures of gas; and, finally, of the mixtures of gas with combustible dust. The study of all these systems is connected with that of the gases themselves.

§ 2. Explosive Gases.

1. There exists a certain number of definite gases, capable of transforming themselves with explosion under the influence of a shock, sudden compression, heating, the electric spark, etc. Such are ozone and the oxygenated compounds of chlorine, which explode through sudden compression or heating. These bodies are characterised by the fact that their formation, either from ordinary oxygen, as in the case of ozone, or from their elements, as in the compound gases, takes place with absorption of heat.

This last characteristic belongs also to other gases, whose explosive decomposition could not be determined for a long time, such as the oxygenated compounds of nitrogen, acetylene, and some other hydrocarbon gases, arseniuretted hydrogen, cyanogen, the vapour of hydrocyanic acid, cyanogen chloride, the vapour of carbon disulphide. Latterly, however, the author has succeeded in making gases of this kind explode under the influence of mercury fulminate (p. 66).

2. The heat liberated by the decomposition of explosive gases is known. It is precisely equal to the heat absorbed in formation (p. 115). Starting from this datum, we can then calculate the pressure and the temperature developed by the explosion according to Mariotte's and Gay-Lussac's laws, and

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by employing the specific heats of the gaseous elements measured at the ordinary temperature. Let us note that here there can be no question of dissociation, since the products of the explosion are elementary gases.

Relying on these principles, the heat liberated, the temperature produced, and the pressure developed for ozone and hypochlorous gas, will first be given. As regards chlorous and hypochlorous gas, no measurement has been taken up to now. A summary of the results referring to nitric oxide, cyanogen, and acetylene will be added.

3. Ozone is changed into ordinary oxygen at the ordinary temperature. This transformation is all the more rapid according as we operate on a mixture of oxygen and ozone richer in ozone, for the latter has never been isolated in a state of purity.[1]

It is accelerated with the temperature and becomes explosive under the influence of sudden compression.[2] The heat liberated is equal to 14·8 Cal. for 24 grms. of ozone, occupying 11·16 lit. or 29·6 Cal. for the molecular weight, $Oz = O_3$ (48 grms.), according to the author's experiments,[3] that is, ·616 Cal. per kgm. of substance.

The specific molecular heat of oxygen being equal to 6·95 for 32 grms. (or O_2) at constant pressure, if we suppose this specific heat to be invariable, the temperature attained by pure ozone when being transformed into oxygen would then be 2840° at constant pressure. At constant volume the specific molecular heat is 5·0 for O_2, and the heat liberated reaches 29·9 Cal. Consequently, the specific heat being supposed constant, the temperature produced would be 3987°.

The pressure developed at constant volume, calculated according to this datum, would be equal to 23·4 atm.

Such are the characteristic data of ozone, supposing it to be pure and taken under the normal pressure. If this be dwelt upon, it is because this transformation represents a typical case in the theory of explosive bodies, since it is only a question of a simple gas changing as regards condensation.

In practice, since pure ozone has never yet been obtained, the transformation is effected in a mixture of ozone and ordinary oxygen. Let us give, moreover, the calculation of the pressure developed for a mixture capable of supplying after transformation a weight of oxygen proceeding from the ozone equal to a sixteenth of the total weight (6·2 hundredths), a mixture which can be easily prepared under ordinary circumstances with the author's apparatus (p. 220).

[1] Upon the rapidity of the transformation, see "Annales de Chimie et de Physique," 5e série, tom. xiv. p. 361, and tom. xxi. p. 162.

[2] Chappuis et Hautefeuille, "Comptes rendus des séances de l'Académie des Sciences," tom. xci. p. 522.

[3] "Annales de Chimie et de Physique," tom. x. p. 152

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The heat liberated is always the same for a given weight of ozone, but it is distributed between the oxygen derived from it, and the excess of the same gas which pre-existed. Consequently, the temperature produced at constant volume will be 245°, and the pressure developed about 1·9 atm.

4. Hypochlorous acid explodes under the influence of a temperature above 60°, or under the influence of a spark, shock, etc.

Thus it liberates 7·6 Cal. by Cl_2O = 43·5 grms., occupying 11·6 lit. or 15·2 Cal. for the molecular weight (87 grms.). $Cl_2O = Cl_2 + O$ liberates 15·2 Cal. at constant pressure, or 175 cal. per gramme of substance.

The specific heat of O being 3·5 and that of Cl_2 8·6, the sum is 12·1 at constant pressure, and the temperature developed in the final mixture of the elements in consequence of their separation will be then $\frac{15{,}200}{12{\cdot}1} = 1256°$.

At constant volume the sum of the specific heats of the elements is reduced to 10·1, and the heat developed rises to 15·5 Cal. The temperature produced rises then to 1530°, and the pressure calculated to 9·9 atm.

5. It has been deemed useful to give these results, since they are typical, owing to the gaseous character of the components and products and the elementary nature of the latter. From the same point of view, it is also interesting to mention the explosions of nitric oxide, acetylene, and cyanogen, although they only take place under the influence of mercury fulminate.

6. The decomposition of nitric oxide into elements, as it is brought about by fulminate (p. 72), becomes complicated, owing to the combustion of carbonic oxide produced by the detonation. If it could be produced isolated, it would develop less pressure than pure ozone. In fact, we arrive at the following figures:—

Heat liberated,

$$Q = + 21{\cdot}6 \text{ Cal. for NO (30 grms.)};$$

temperature developed at constant volume,

$$t = 4204°;$$

pressure produced,

$$p = 16{\cdot}4 \text{ atm.}$$

7. The detonation of acetylene, also induced by fulminate (p. 69), gives rise to the following effects:—

Heat liberated,

$$Q = 61 \text{ Cal. for } C_2H \text{ (26 grms.)};$$

temperature developed at constant volume,

$$t = 6220°;$$

pressure produced,

$$p = 23{\cdot}8 \text{ atm.}$$

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8. The detonation of cyanogen caused by fulminate (p. 71) corresponds to the following effects:—

Heat liberated,

$$Q = 74{\cdot}5 \text{ Cal. for } C_2N_2 \text{ (52 grms.)};$$

temperature developed at constant volume,

$$t = 7600°;$$

pressure produced,

$$p = 28{\cdot}8 \text{ atm.}$$

In these calculations it is supposed that the molecular heat of solid carbon is equal to that of gaseous oxygen at constant volume.

We see from these figures that the temperature developed and the pressure produced by acetylene and cyanogen would exceed the effects produced by all other explosive gases, even if we take into consideration the solid state of the carbon.

§ 2. Detonating Gaseous Mixtures.

1. Chlorine and oxygen are the only simple gases which can supply explosive gaseous mixtures by their association with combustible gases, hydrogenated or carburetted. Among the compound gases, the chlorine and nitrogen oxides share this property.

2. In the following table the characteristic data have been given for the principal detonating gaseous mixtures constituted by these various gases, whether combustive or combustible.

Here the heat liberated results from the formation of certain compound bodies; consequently the maximum pressure, calculated theoretically, might be considerably diminished in practice, owing to dissociation. It might also be diminished owing to the variation of the specific heats. We shall revert to this subject later on, but first give the theoretical values.

3. According to this table, the maximum work which can be accomplished by one kgm. of the various explosive gases, work which is in proportion to the heat liberated, that is, the potential energy of these mixtures, varies only from single to double for gases containing carbon and hydrogen mixed with pure oxygen (the water being supposed to be gaseous).

Moreover, this work is nearly the same for the various hydrocarbon gases.

Such work exceeds, moreover, that of all the solid or liquid explosive compounds taken under the same weight. With hydrogen and oxygen, for instance, it is four times as great as that of ordinary powder, and twice as great as that of nitroglycerin.

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Nature of the Explosive Mixture.	Formulæ referred to Molecular Weight.	Total Molecular Weight.	Products.	Heat disengaged at constant pressure.		Reduced gaseous volume (V°) occupied by 1 kilogram.[2]		Theoretical pressure.[3]
				For Molecular weight.	For 1 kilogram.	Initial.	Final.	
		grms.		Cal.	Cal.	m.c.	m.c.	atm.
Oxygen and hydrogen	$H_2 + O$	18	H_2O liquid	69·0	3833	1·86	0·018	20
			H_2O gas	59·0	3278	1·86	0·24	
Chlorine and hydrogen	$H + Cl$	36·5	HCl gas	22·0	603	0·61	0·61	18
Nitrogen monoxide and hydrogen	$N_2O + H_2$	46	$N_2 + H_2O$ liquid	89·6	1948	0·97	0·48	25
			$N_2 + H_2O$ gas	79·6	1730	0·97	0·97	
Nitric oxide and hydrogen[1]	$NO + H_2$	32	$N + H_2O$ liquid	90·6	2831	1·395	0·35	20
			$N + H_2O$ gas	80·6	2519	1·395	1·05	
Carbonic oxide and oxygen	$CO + O$	44	CO_2 gas	68·2	1483	0·78	0·48	24
Carbonic oxide and nitrogen monoxide	$CO + N_2O$	72	$CO_2 + N_2$	88·8	1233	0·62	0·62	28
Marsh gas and oxygen	$CH_4 + O_4$	80	$CO_2 + 2H_2O$ liquid	213·5	2669	0·84	0·28	34
			$CO_2 + 2H_2O$ gas	193·5	2419	0·84	0·84	
Acetylene and oxygen	$C_2H_2 + O_5$	106	$2CO_2 + H_2O$ liquid	318·1	3001	0·74	0·43	45·5
			$2CO_2 + H_2O$ gas	308·1	2907	0·74	0·63	
Acetylene and nitric oxide	$C_2H_2 + 5NO$	176	$2CO_2 + H_2O$ liquid + 5N	416·1	2364	0·76	0·57	44
			$2CO_2 + H_2O$ gas + 5N	406·1	2307	0·76	0·70	
Ethylene and oxygen	$C_2H_4 + O_6$	124	$2CO_2 + 2H_2O$ liquid	341·4	2753	0·72	0·36	42
			$2CO_2 + 2H_2O$ gas	321·4	2592	0·72	0·72	
Ethylene and nitric oxide	$C_2H_4 + 6NO$	208	$2CO_2 + 2H_2O$ liquid + 6N	571	2745	0·75	0·54	48
			$2CO_2 + 2H_2O$ gas + 6N	551	2649	0·75	0·75	
Ethane and oxygen	$C_2H_6 + O_7$	142	$2CO_2 + 3H_2O$ liquid	389·3	2742	0·71	0·31	38
			$2CO_2 + 3H_2O$ gas	359·3	2530	0·71	0·79	
Ether vapour and oxygen	$C_4H_{10}O + O_{12}$	266	$4CO_2 + 5H_2O$ liquid	655·7	2465	0·59	0·34	45
			$4CO_2 + 5H_2O$ gas	605·7	2277	0·59	0·75	
Benzene vapour and oxygen	$C_6H_6 + O_{15}$	318	$6CO_2 + 3H_2O$ liquid	783·2	2463	0·60	0·42	45
			$6CO_2 + 3H_2O$ gas	753·2	2369	0·60	0·63	
Cyanogen and oxygen	$C_2N_2 + O_4$	116	$2CO_2 + N_2$	262·5	2263	0·58	0·58	51
Cyanogen and nitric oxide	$C_2N_2 + 4NO$	172	$2CO_2 + 6N$	348·9	2028	0·65	0·65	45·5

[1] This reaction does not take place directly. It has been calculated for comparison, but would no doubt be effected by a fulminate cap. [2] This volume is referred to 0° and 760 mm. The water is supposed gaseous; formulæ containing this volume should in general only be used above 100°. [3] This pressure is calculated according to Mariotte and Gay-Lussac's laws; the heat disengaged has been calculated for constant volume. The following values for specific heats have been taken: 7·2 for H_2O = 18 grms.; 4·8 for HCl = 36·5 grms.; 7·2 for CO = 28 grms.; 4·8 for N_2 = 28 grms. The explosive mixture is supposed to have been prepared at atmospheric pressure.

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With hydrocarbon gases it is three times that of powder, and one and a half times as much as that of nitroglycerin. However, the advantages which might result from the potential energy of explosive gaseous mixtures compared to that of solids and liquids are counterbalanced in practice by the difficulties arising from the greater volume of the gaseous mixtures and the necessity of keeping them in resisting envelopes. From this point of view of the potential energy of gaseous mixtures, referred to the unit of weight, no combustive, generally speaking, rivals pure oxygen, seeing that every other oxidising compound contains inactive elements (useless weight), which share the heat without supplying sufficient compensating energy at the moment of the destruction of the oxidising compound.

4. We must remark that the theoretical pressures calculated for the various explosive mixtures scarcely vary, except from single to double, these being limits which we shall find by-and-by, between the pressure really observed, notwithstanding the diversity of composition and the condensation of the gases taken into consideration.

5. Moreover, the pressures calculated are purely theoretical, and only intended to serve as terms of comparison.

In fact, the figures measured by observers are much lower, which is explained either by the short duration of the state of integral combination which seems to correspond to the explosive wave, or by the inaccurate estimation of the specific heats employed in the calculations, or, finally, by dissociation.

Let us follow up this question.

It suffices to admit the existence of a certain dissociation in order to reduce the pressures by one-half, or even one-third, of the calculated values.

Nevertheless, the rapidity of propagation of the explosive wave as it has been measured (p. 101) seems to indicate that at the moment of its production the explosive system contains all the heat liberated by an integral combination. The propagation of the wave is, however, so rapid that the pressure observed probably corresponds in every kind of apparatus to a system which is already partially cooled, and it is this reduced pressure which seems to correspond to the case of ordinary combustion. We might also explain the results observed by accepting the variation of specific heats, especially if we double the mean specific heat of water vapour or of carbonic acid.[1]

Experience has not yet expressed a definite opinion respecting these different manners of conceiving the phenomenon. It tends, however, to show that the part played by dissociation had been exaggerated at first.

6. Let us now cite the figures really observed for pressures subject to the reservations just named.

[1] See "Essai de Mécanique Chimique," tom. i. pp. 344 et 346.

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According to Bunsen's experiments,[1] made by raising a valve loaded with a weight, a mixture of carbonic oxide and oxygen burnt at constant volume only develops 10·3 atm., instead of 24 as calculated. The number observed would correspond to the combination of only one-third of the mixture on the hypotheses of dissociation. Such a calculation is, however, based on the employment of far too low a specific[2] heat for the carbonic acid.

A mixture of hydrogen and oxygen, burnt at constant volume, develops also, according to Bunsen, 9·6 atm. instead of 20 atm. as calculated. The number observed would correspond again to the combination of a third of the mixture on the hypotheses of dissociation, but it is subject to the same objection for the specific heat.

Mallard and Le Châtelier arrived at approximate experimental values by their measurements, based on the employment of a metallic manometer; say 8·6 atm. for the mixture of carbonic oxide and oxygen, 9·2 atm. for the mixture of hydrogen and oxygen, 14 atm. for methane and oxygen, 8 atm. for chlorine and hydrogen, etc.

The following are the numbers observed by the author and M. Vieille with the principal detonating mixtures, by another method based on the registration of the pressures by means of a movable piston:—

	atm.
Hydrogen and oxygen: $H_2 + O$	7·7 atm. to 9·6[3]
Hydrogen and nitrogen monoxide: $H_2 + N_2O$ ...	... 11·1
„ nitrogen and oxygen: $H_2 + N_2 + O$ ...	... 8·2
„ „ „ : $H_2 + 2N_2 + O$ ...	... 7·4
Carbonic oxide and oxygen: $CO + O$	... 9·4
„ „ and nitrogen monoxide: $CO + N_2O$ ...	... 9·7
„ „ nitrogen and oxygen: $CO + N_2 + O$ ...	... 7·7
„ „ „ „ : $CO + N + O$ ...	... 8·0
„ „ hydrogen and oxygen: $CO + H_2 + O_2$	... 7·8
„ „ „ „ : $2CO + H_2 + O_2$	... 8·3
Methane and oxygen: $CH_4 + O_4$	... 13·6
Acetylene and oxygen: $C_2H_2 + O_5$	... 13·7
Ethylene and oxygen: $C_2H_4 + O_6$	... 13·8
Ethane and oxygen: $C_2H_6 + O_7$	... 11·9
Ethylene, hydrogen, and oxygen: $C_2H_4 + H_2 + O_7$ ...	... 13·3
Cyanogen and oxygen: $2CN + O_4$	... 19·5
Cyanogen, nitrogen, and oxygen: $2CN + N_2 + O_4$ ...	... 15·6

Cyanogen gives the maximum pressure according to theory. However, the values observed are only two-fifths of the theoretical values for hydrogen, carbonic oxide, and methane. They are reduced to about a third for the other hydrocarbons and for cyanogen.

It results from these indications that the real relations of the

[1] "Annales de Chimie et de Physique," 4ᵉ série, tom. xiv. p. 446. 1868.

[2] See the author's remarks on this point ("Annales de Chimie et de Physique," 5ᵉ série, tom. xii. p. 306).

[3] According as the experiment was made in a chamber of 300 cc. or 4 litres.

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pressures observed do not differ very much from the theoretical pressures, so that, if necessary, the latter may be employed in the comparisons, at least for a first approximation.

7. By replacing pure oxygen by its mixture with nitrogen, that is, by atmospheric air, in order to effect the combustion of the gases and vapours, we obtain systems which are very interesting in their applications. In fact, it is a similar mixture of air and methane which constitutes the fire-damp so much dreaded in mines.

A similar mixture, composed of air and coal gas, has often given rise to serious accidents in houses and sewers.

The vapour of ether, carbon disulphide, and petroleum spirit, associated with air, have more than once produced fires and explosions in manufactories and laboratories. Let us now examine more closely the effects of this substitution of air for oxygen.

8. It does not change the heat liberated, and consequently it does not affect the maximum work which can be developed by a given weight of the combustive body.

9. On the contrary, it modifies the pressures, and that in two ways. In fact, at first sight it may be conceived that the theoretical pressures should decrease by one-half, or even more, owing to the necessity of heating the nitrogen, and even the excess of oxygen, which lowers the temperature. For instance, hydrogen mixed with five times its volume of air would not develop, according to theory, more than 8·5 atm., instead of 20 atm., and only 5·1 atm. with ten times its volume of air.

10. These figures are still above the real values, for the same reasons that lower the pressures with pure oxygen, that is to say, on account of dissociation, or rather, the increase of the specific heats (p. 388).

However, the influence of these causes is limited by the lowering of the temperature. Thus, according to Bunsen, one-half of the mixture of carbonic oxide and oxygen would burn, instead of one-third, as soon as the temperature falls below 2560°. Below 1146° the quantity burnt would again increase, and continue to do so until total combustion took place. Nevertheless, the last figures must be looked upon as doubtful. In fact, they have been derived from observed pressures, assuming the specific heats to be constant, which is not admissible;[1] now the effects observed can be explained equally by the variation of the specific heats, a variation which cannot be disputed for compound gases.

For instance, since the specific heat of carbonic acid increases with the temperature, the gaseous mixture which contains it is brought to a lower temperature by a given quantity of heat,

[1] See "Annales de Chimie et de Physique," 5ᵉ série, tom. xii. p. 305.

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and the pressure developed is diminished to the same extent. The difference is, however, diminished by the introduction of a certain quantity of inert gas, which tends of itself to lower the temperature. The pressure will even be reduced proportionately still more for such mixtures than for explosive mixtures containing no inert gases.

11. This is confirmed by experience. As far back as 1861, Hirn measured the pressure developed by the combustion of air mixed with one-tenth of its volume of hydrogen, and he found 3·25 atm., instead of 5·14 atm.. The reduction would be about one-third, instead of being greater than the half, as with pure oxygen.

Mallard made similar observations[1] on various mixtures of air and combustible gases.

Finally may be cited the recent experiments of Mallard and Le Châtelier on the pressures developed by mixtures of air and methane, and also on mixtures of air and coal gas.[2] The measurements of these authors were effected by means of a hollow spring, which served as a registering manometer and communicated with a combustion chamber of 4 litres capacity.

			atm.
0·94	(CO + O)	mixed with 0·06 of inert gas (nitrogen and water vapour)	8·6
0·31	(CO + O)	„ 0·66 of CO_2, 0·02, 0·01 water vapour	6·0
0·955	(H_2 + O)	„ 0·03 N + 0·015 water vapour	9·2
0·67	„	„ 0·32 O + 0·01 „	8·3
0·65	„	„ 0·34 H + 0·01 „	8·1
0·49	„	„ 0·49 O + 0·02 „	7·2
0·32	„	„ 0·67 H + 0·01 „	6·3
0·33	„	„ 0·65 N + 0·02 „	6·3
0·19	„	„ 0·54 H + 0·25 N + 0·02 water vapour	5·15
0·17	„	„ 0·14 H + 0·69 N + 0·02 „	5·0
0·95	(H + Cl)	„ 0·03 H + 0·02 water vapour	8·1
0·74	„	„ 0·25 Cl + 0·01 „	7·1
0·51	„	„ 0·47 H + 0·02 „	7·0
0·41	„	„ 0·59 H + 0·01 „	6·0

The detonating mixture with a methane base ($CH_4 + O_4$), mixed with three times its volume of air, gave pressures approaching 7 atm.

With the same mixture, when pure, the figure rose to 14 atm.

The following is a table of some observations which M. Vieille and the author made by means of a movable piston :—

I. Mixture of two combustible gases.

	atm.
$CO + H_2 + O_2$	7·8
$2CO + H_2 + O_5$	8·3
$C2H_4 + H_2 + O_7$	13·3

[1] "Annales des Mines," tom. vii. 1871.

[2] "Journal de Physique," 2e série, tom. i. p. 182.

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II. Mixture of detonating gases with an inert gas.

	atm.
$H_2 + O + N_2$	8·2
$H_2 + O + N_4$	7·4
$H_2 + N_2 + N_2O$	9·5
$CO + O + N_2$	7·7
$CO + O + N$	8·0
$CN + O_2 + N$	15·6

From these various measurements very important results may be deduced for the theoretical study of the temperatures of combustion, specific heat and dissociation; but this discussion would lead us too far, and it suffices to cite the above-mentioned figures as terms of comparison.

12. The temperature may be lowered to a limit at which the inflammation ceases to propagate itself, and this limit is interesting, since it is the same as that which commences to produce the inflammation of the mixture in an adverse sense.

We have here two distinct notions to define: the composition limit,[1] and the temperature limit.

13. *Composition limit of inflammability.* An explosive gaseous mixture ceases to burn when the relative proportion of one of its components falls below a certain proportion. For instance, 3 vols. of electrolytic gas, formed by 1 vol. of oxygen and 2 vols. of hydrogen, cease to ignite when mixed with 27 vols. of oxygen or with 24 vols. of hydrogen.

A similar volume of water vapour, above 100°, also prevents ignition. It is the same at the ordinary temperature with 18 vols. of nitrogen, 12 vols. of carbonic oxide, 9 vols. of carbonic acid, 6 vols. of ammonia gas, hydrochloric acid or sulphurous acid, etc.

Three vols. of gas, formed by 1 vol. of oxygen and 2 vols. of carbonic oxide, ceases to ignite when mixed with 10 vols. of carbonic oxide or 29 vols. of oxygen.

The mixture of methane with air only gives rise to an exact combustion when it is formed by 9·5 vols. of air for 1 vol. of methane. It ceases to burn where the proportion of air exceeds 17 vols. to 20 vols. These are very important data, owing to the presence of fire-damp in mines.

The combustion is incomplete near the limits of inflammability.

These limits, however, vary considerably according to the process of inflammation, and, above all, with the temperature and mass of the body in ignition, which serves to produce the combustion.

They also vary according to the nature of the electric spark, when the latter is employed to produce ignition, the spark produced with the aid of a condenser being much more efficacious

[1] See "Essai de Mécanique Chimique," tom. ii. pp. 73 et 343.

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than ordinary sparks. All this can be easily understood, since the igniting agent propagates the combustion around itself in a sphere which is more or less extended, according to the quantity of heat it supplies itself.[1]

Hence variations and strange phenomena result in a mixture limit, the mixture becoming filled with small disseminated flames, which are propagated hither and thither, and whose production precedes the state of general combustion. These curious effects have been the object of special study by Schlœsing and Demondésir.

The singular phenomena witnessed in the Solfatara at Pozzuoli could also be cited. Towards certain points, especially in a depression, vaporous wreaths are liberated, irregular jets of water vapour mixed with a trace of sulphuretted hydrogen. It suffices to bring near them some ignited body, such as tinder, when the sulphuretted hydrogen burns in contact with the air in which it is disseminated, with the production of a cloud which gradually extends and propagates itself all round to a considerable distance.[2]

The easy ignition of sulphur and its compounds is a great factor in this circumstance, but has nothing to do with explosive phenomena.

From the point of view of mechanical effects produced by a detonating mixture, the rapidity with which the ignition is propagated is very essential, the latter taking place sometimes by ordinary combustion, and sometimes owing to a real explosive wave, which proceeds with incomparably greater rapidity (pp. 49, 55, 88, 90). Now, the limits of composition at which the explosive wave ceases to be produced are far higher than those which correspond to simple ignition. This is a very important result as regards applications (see p. 110). The limit of inflammability, and especially the more or less easy propagation of the inflammation, is influenced by the pressure, which increases the mass of heated matter in a given time and extent, and consequently checks the influence of cooling.

The limit is also influenced by the initial temperature of the mixture. That is, the excess of temperature of the body which produces ignition above that of the inflammable mixture ought to be less according as the latter mixture is raised beforehand to a higher temperature (see p. 64).

Generally speaking, in order that the propagation of the combustion may take place, it is necessary that the heat liberated by the ignition of the first parts should be sufficient to reproduce in the adjoining portions the initial temperature at which the combustion commenced.

[1] "Essai de Mécanique Chimique," tom. ii. pp. 338, 343 et 346.

[2] Melloni et Piria, "Annales de Chimie et de Physique," 2e série, tom. lxxiv. p. 331.

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This is also a question in which there intervene, at the same time, the quantities of heat liberated, the specific heats of the products of combustion, and those of the gases in excess with which these products are mixed. The variation of the specific heats of the compound gases with the temperature enters then into consideration here. If this were not the case, it would always be easy to calculate *à priori* the temperature limit. We will cite various facts respecting the latter temperature.

14. *Temperature of inflammation.* This temperature, which corresponds to the minimum of work required to produce the reaction, presents a certain amount of interest as regards applications. It has been frequently studied since the time of H. Davy. On this point, the following are the most recent data, due to Mallard and Le Châtelier[1]:—

2 vols.	H	+ 1 vol.	O			...	550° to 570°
1 „	H	+ 2 „	O			...	530°
1 „	air	+ 2 „	H			...	530° „ 570°
2 „	air	+ 1 „	H			...	550°
1 „	O	+ 2 „	H	+ 3 vols.	CO_2	...	560° „ 590°
1 „	O	+ 5 „	CO			...	630° „ 650°
1 „	O	+ 2 „	CO			...	650°
2 „	O	+ 1 „	CO			...	650° „ 660°
1 „	O	+ 2 „	CO	+ 3 vols.	CO_2	...	700° „ 715°
2 „	air	+ 1 „	CO	+ 3 „	CO_2	...	715° „ 725°
2 „	O	+ 1 „	CH_4			...	650° explosion 600° slow combustion
1 „	O	+ 2 „	CH_4			...	650° to 660°
1 „	CH_4	+ 9 „	air			...	lower than 750°

It is remarkable how the ignition temperature of detonating mixtures formed by the association of oxygen either with hydrogen, carbonic oxide, or with methane, is but slightly modified by the introduction of even a considerable volume of foreign gases. The same happens at least as long as the limits at which the mixture ceases to burn are not approached.

Nevertheless, the addition of an equal volume of carbonic acid has a greater influence on carbonic oxide than on hydrogen, as if the very products of the combustion of the mixture exercised a special influence on the ignition temperature.

The authors also observed that there exist very notable differences between the different intervals of time required to ignite a gaseous mixture brought to a given temperature. Thus the mixtures containing hydrogen or carbonic oxide ignite immediately, whilst a certain time is required for the mixtures of methane with air or oxygen. Hence it is that a bar of iron when brought to a red heat does not ignite these mixtures, since the gases escape before having been subjected to the influence of this temperature for a sufficient time. These

[1] "Comptes rendus des séances de l'Académie des Sciences," tom. xci. p. 825.

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observations are very important as regards the study of fire damp.

15. The oxidation of gases and of organic substances heated to 300° or 400° may be slowly effected, with a phosphorescent glow, only visible in the dark, such as is seen when ether or absolute alcohol is poured on a red-hot brick. The very products of the oxidation are thus changed, as aldehyde is formed by means of ether. If, however, these reactions are prolonged, especially in the presence of a porous body of small mass, the oxidation is rendered more active by the very heat it liberates, and it may raise the temperature of the system up to the sudden and explosive degree of ignition. This happens sometimes with cotton impregnated with oil, with slowly burning tinder, with brown coal, etc. It has been observed that in manufactories and powder magazines serious accidents have been caused by this cause of ignition, that is to say, due to the elevation of temperature, owing to slow oxidation, which gradually accelerates.

16. Gases containing sulphur ignite at much lower temperatures than hydrocarbon gases, from 250° for example. With reference to this matter may be instanced the following experiment. Taking two flat dishes, ether is poured into one and carbon disulphide into the other. If, then, a piece of red-hot coal, but emitting no flame, be introduced into the ether it is extinguished; but if it be only rolled in it so as to make the superficial incandescence disappear, and we introduce it at once into the carbon disulphide, the latter becomes ignited and can then ignite the ether placed beside it.

Certain compounds, such as chlorinated and brominated acetylene, ignite spontaneously in contact with air in consequence of analogous phenomena. The same is the case with several phosphoretted compounds.

17. Let us now return to the question of pressures. Instead of burning a combustible gas by pure oxygen, we should be inclined to expect some advantage arising from nitrogen monoxide or nitric oxide, seeing that by their own decomposition these gases supply an additional volume of nitrogen and a supplementary quantity of heat. Nevertheless these advantages are nearly compensated by the necessity of heating the nitrogen (Table on p. 387).

18. It would be quite another thing if we only considered the total work, for since this is proportional to the heat liberated it is increased with nitrogen monoxide and nitric oxide.

There also exist certain oxidising solids, such as potassium chlorate, which supply more heat than free oxygen. On the other hand, pure oxygen produces more than potassium nitrate, and more than most of its liquid or solid compounds.

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The heating of the elements, excepting oxygen, consumes, moreover, a portion of this work, and this limits the elevation of the temperature and pressure, as has just been said. Moreover, let us note that the storage of oxygen in its compounds is always very costly.

Hence it can scarcely be expected that economical engines can be invented which will derive their motive power from solid explosive substances, such as ordnance powder, as Papin once imagined. Nevertheless, such machines, if they could be controlled, would perhaps be applicable to special conditions, where the reduction of the volume of the apparatus would be of paramount consideration.

19. From these facts and considerations it results that the employment of gaseous mixtures appears more economical in machines than that of other explosive mixtures, solid or liquid. In fact, gas engines are based on the combustion of coal gas by air. However, in this case, the combustible and the combustive are introduced from without and the products are gradually discharged, and this limits the volume of the apparatus.

20. The gaseous mixtures we have under consideration have been supposed to be produced under atmospheric pressure; the theoretical pressures which they then develop, being comprised between 18 atm. and 51 atm., are far removed from the pressures developed by most explosives, whether solid or liquid. The effective pressures are even far less, since they do not exceed 20 atm. (p. 389), a result which differs from the opinions entertained by most persons during the siege of Paris.

21. It would be advantageous to compress gaseous explosive mixtures beforehand, but the pressures developed would become comparable to those of solid or liquid mixtures only by employing enormous compressions capable of reducing the initial volume of the mixture to one-hundredth, or a still smaller fraction, that is by bringing it to a density equal to that of solids or liquids. Apart from the practical difficulties attending such a compression, it would result in liquefying most of the hydrocarbon gases without liquefying the oxygen at the same time, which would destroy the homogeneity of the explosive mixture and the possibility of its immediate ignition.

§ 4. Mixture of Liquefied Gases and Analogous Liquids.

In this case certain advantages could be obtained by the employment of nitrogen monoxide in the liquid state or of liquid nitric peroxide, a compound which may be likened to a liquefied gas owing to its great volatility.

The oxides of chlorine, whose combustive properties would be extremely valuable if they were not too dangerous to manipulate,

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in consequence of their liability to explode spontaneously, need not be considered. The oxides of nitrogen, on the contrary, are stable in the cold.

Now, the liquid oxides of nitrogen can be associated with liquefied hydrocarbons in hermetically closed vessels. Thus we obtain mixtures whose theoretical explosive force is comparable to that of the most energetic compounds, such as nitroglycerin or the mixtures of potassium chlorate with gun-cotton or potassium picrate.

Such mixtures of liquefied gases formed by the oxides of nitrogen do not detonate directly, but may do so under the influence of primings of mercury fulminate, and this makes up the resemblance between such mixtures and dynamite.

During the siege of Paris the author made some trials of this kind with *liquid* nitrogen monoxide.

Recently M. Turpin thought of having recourse to nitric peroxide, which is more easily handled, since it remains liquid up to about 26° and may then be easily mixed with various combustible compounds, such as carbon disulphide, ether, petroleum spirit, etc. This is the base of the panclastites patented by this ingenious inventor.

It is not yet known how far such a volatile body as nitric peroxide, the vapour of which it is so dangerous to breathe, and which is so corrosive, could be applied. It may, however, be noted that this body nearly represents liquid oxygen, the loss of energy being almost *nil* in its formation (p. 128). Its explosive decomposition presents the disadvantage of heating the nitrogen which does not intervene in the combustion.

The study of mixtures of this kind presents very great variety, but the reactions they develop are but imperfectly known, except as regards the systems which correspond to total combustion. We shall therefore limit ourselves to these.

The following figures will serve to show the theoretical energy of the mixtures formed by liquid nitrogen monoxide and nitric peroxide.

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Explosive material.	Heat disengaged by 1 grm. water gaseous.	Reduced volume of the gases formed.[1]	Permanent pressure at 0° under density of charge $\frac{1}{n}$.[2]	Theoretical pressure at moment of explosion.
	cal.	m.c.	atm.	
Nitrogen monoxide and liquefied ethane . $C_2H_6 + 7N_2O$ . .	1356	0·79	$\frac{590}{n - 0·16}$	$\frac{21,700}{n}$
Ethylene[3] or analogous liquid hydrocarbons . $C_2H_4 + 6N_2O$ . . .	1418	0·76	$\frac{610}{n - 0·12}$	$\frac{22,200}{n}$
Liquefied acetylene[3] . $C_2H_2 + 5N_2O$ . . .	1564	0·73	$\frac{640}{n - 0·07}$	$\frac{24,300}{n}$
Liquid benzene . . . $C_6H_6 + 15N_2O$ . . .	1839	0·73	$\frac{640}{n - 0·07}$	$\frac{19,600}{n}$
Liquefied cyanogen[3] . $C_2N_2 + 4N_2O$ . . .	1416	0·69	$\frac{690}{n}$	$\frac{26,900}{n}$
Liquid carbon disulphide $CS_2 + 6N_2O$	1012	0·59	$\frac{590}{n}$	$\frac{15,350}{n}$
Liquid nitrobenzene . $2C_6H_5NO_2 + 25N_2O$.	1346	0·71	$\frac{630}{n - 0·04}$	$\frac{22,100}{n}$
Liquid nitric peroxide and liquid[4] . . . $2C_2H_6 + 7NO$ . . .	1794	0·79	$\frac{644}{n - 0·28}$	$\frac{23,800}{n}$
Liquefied cyanogen . . $C_2N_2 + 2NO_2$ . . .	1800	0·62	$\frac{620}{n}$	$\frac{25,400}{n}$
Liquid nitrobenzene . $4C_6H_5NO_2 + 25NO_2$.	1568	0·60	$\frac{480}{n - 0·12}$	$\frac{20,000}{n}$
Liquid carbon disulphide $CS_2 + 3NO_2$[5] . . .	1129	0·47	$\frac{470}{n}$	$\frac{15,040}{n}$
Nitroglycerin	1460	0·72	$\frac{480}{n - 0·20}$	$\frac{19,080}{n}$

[1] This volume ought really to be multiplied by $(1 + \alpha t)$ to render the water actually gaseous at t.

[2] One grm. in n cubic centimetres; water liquid. These figures are only valid when n is sufficiently large for the carbonic acid not to be liquefied, or in the case of carbon disulphide, the sulphurous acid.

[3] Favre found the heat of liquefaction of N_2O = 44 grms. to be = 4·4 Cal. This figure has been taken for the other liquefied gases.

[4] Nitric peroxide is incompatible either with ethylene or benzene.

[5] Turpin employed barely half the proportion of nitric peroxide indicated here; this gave rise to incomplete combustion with deposition of sulphur.

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§ 5. Gas and Combustible Dusts.

1. A gas may form explosive mixtures, not only by its association with another gas, but also with a solid or liquid dust. Hence we obtain systems of a very special order. Their explosive nature may easily be conceived, seeing that these systems, when once ignited, give rise to sudden expansion, accompanied by an increase of pressure. However, the explosion of such a system is necessarily slower than that of a purely gaseous mixture, since the propagation of the reaction only takes place as each solid particle is reached by the incandescent gases arising from the combustion of the neighbouring particles. Hence we may conceive the influence exercised by the slightest trace of combustible vapour or gas already mixed with air in facilitating ignition.

2. Explosions of this kind have been observed in coal mines, in flour mills and warehouses, and in places containing sulphur in the form of an impalpable powder.

The clouds formed by petroleum vapours and other volatile hydrocarbons have also given rise to similar explosions in cellars or magazines, or even in the open air, but in this case the effects are of a mixed character, owing to the peculiar vapour tension of these hydrocarbons, a portion of which should be considered as gaseous in these mixtures.

3. Reference will only be made to mixtures formed by air associated with a combustible dust. Let us first define the limits which correspond to the maximum effect with mixtures of air and combustible dust, supposed to be effected in suitable proportions at the moment of explosion.

(1) *Mixtures of air and charcoal.* One cubic metre of air may by its oxygen generate 208 litres of carbonic acid reduced to 0° and 760 mm. The same volume of air would burn 112 grms. of pure carbon. Now such a system, namely, an intimate and as uniform a mixture as possible of air and carbon in the form of powder would develop a theoretical pressure of 15·5 atm. if it were burnt at constant volume. If the quantity of charcoal were doubled (224 grms.) and the whole could be changed into carbonic oxide, we should obtain 416 litres of the latter gas, and the pressure developed would be 6·7 atm.

If necessary, carbonaceous dusts may be assimilated to carbon for similar effects.

At any rate we see that the maximum limit of theoretical pressures which can be developed by the combustion of a carbonaceous dust is similar to the pressures developed by fire-damp itself.

(2) *Mixtures of air and starch.* Let us take it to be starch dust which, to facilitate calculation, we may substitute for

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flour: 1 cubic metre of air would burn 255 grms. of starch ($C_6H_{10}O_5$), developing a theoretical pressure rather above that which carbon would produce (owing to the aqueous vapour).

(3) *Mixtures of air and sulphur.* Finally 1 cubic metre of air would burn about 300 grms. of powdered sulphur, developing a pressure of 11 atm.

4. The limits we have just defined presuppose a uniform distribution of the dust in the air, which, however, can only be realised under very special conditions of movement and division of the dust.

It is, moreover, difficult to reproduce them by experiment.

Such systems, moreover, supposing them to be produced instantaneously, cannot exist in the same state, without violent agitation, since the action of gravity tends to separate the components, contrary to what occurs with systems formed by the mixture of two gases.

In a system consisting of gas and dusts the relative proportions are therefore continually modified by time, as are also the combustible properties of the system which can only maintain their maximum for a very short period.

5. On the contrary, however, combustible dusts mixed with air remain inflammable far beyond the combustible limits of purely gaseous mixtures, and one single grain in a state of ignition suffices to propagate the flame, either to the neighbouring strata, or to the surface of the surrounding solid bodies.

Such seem to be the most ordinary conditions of the accidents produced by inflammable dusts at the bottom of mines. They are due to a propagated inflammation rather than to a real explosion. Nevertheless, the expansion of the gases is sufficiently sudden to produce violent mechanical effects, which are very dangerous.

6. The propagation of fire in a mixture of air and combustible dust is intensified by the movements of expansions and the projection of gaseous masses, inflamed at the very outset. Hence it is as regards coal-mines that experience has led to attributing a very dangerous part to carbonaceous dust, raised like a whirlwind when a blast is fired, and which propagates fire and asphyxia even to a great distance in the galleries. Thus it has happened that a blast, the flame of which did not extend beyond 4 metres, has propagated combustion through the dust that was raised, to a distance of more than 14 metres, and reached workmen who thought they were out of danger.

Blastings which blow out are especially dangerous in this respect.

At the outset a real amplificatiou of the flame is produced; afterwards it is a simple propagation of the ignition of the dust.

The finer the dust is the more the volume of the initial flame provoking the phenomenon can be limited.

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7. The proportion of volatile substances which coal dust can supply also plays an essential part, for these substances, reduced to vapour by combustion, in their turn promote the propagation of the ignition. This dust, however, only burns in an incomplete manner and by means of a kind of distillation which deprives it of its hydrogen, leaving as a residuum portions of coke adhering to the walls and wood-work. Owing to this fact it is not the mixture of air and dust effected in theoretical proportions which is the most combustible, but a mixture which is richer in carbon, seeing that only the superficial layers of the grains take part in the combustion.

8. Finally, the propagation of the inflammation is effected all the better if the air in the mine already contains a small quantity of some combustible gas, such as methane, the proportion of which is often too feeble for it to form by itself a detonating mixture with the air in the mine.

In mixtures of this kind, even an inert dust, such as magnesia, lowers the limits of combustibility; a mixture containing only 2·75 of fire-damp may thus burn, but in this case the combustion does not propagate itself. This circumstance seems to be due to the storage of heat by the magnesia, which then heats the neighbouring gaseous particles, and consequently lowers their limit of combustibility (p. 393).

Combustible dusts are evidently more efficacious. They increase, moreover, the violence of the explosion produced by fire-damp, owing to the volume of the gases and the supplementary heat they supply. Besides this, they tend to increase the quantity of carbonic oxide which is so dangerous to the mines.

All these circumstances, observed by engineers and managers of mines, have been made the object of methodical experiments by Galloway and Abel in England, and also by Mallard and Le Châtelier in France,[1] in an inquiry recently instituted by the fire-damp commission. For further details the reader is referred to the publications issued by that commission.

[1] "Annales des Mines," Janvier et Février, 1882.

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CHAPTER IV.

DEFINITE NON-CARBURETTED EXPLOSIVE COMPOUNDS.

§ 1.

THE general list of these compounds has been given on p. 368. The only ones which have been the object of sufficiently accurate experiments to speak of them here are—nitrogen sulphide, nitrogen chloride, potassium chlorate, and certain ammoniacal salts of the higher oxygenated acids, such as ammonium nitrate, perchlorate, and bichromate.

§ 2. NITROGEN SULPHIDE: NS.

1. Nitrogen sulphide contains, for 1 equiv. = 46 grms., 32 grms. of sulphur and 14 grms. of nitrogen. Or for 1 kgm., sulphur 696 grms., nitrogen 304 grms. Its density is equal to 2·22. It is solid and crystallised. Heated to 207° it is decomposed, suddenly and explosively, into sulphur and nitrogen.

2. According to the thermal study which we have made of this body (p. 262), its explosive decomposition at constant pressure,

$$NS = SN,$$

liberates + 32·2 Cal. for 46 grms.; at constant volume + 31·9 Cal.

3. It develops 11·16 litres of nitrogen.

This gives for 1 kgm. 694 Cal. and 242·6 litres of nitrogen reduced to 0° and 760 mm.

At the temperature of explosion, sulphur should be regarded as gaseous and even as possessing its theoretical density, which it acquires beyond 800°, according to Troost and Deville. The total volume of the gases for 1 kgm. would then be at the temperature t: 485·2 litres $(1 + at)$.

To calculate the theoretical pressure at constant volume it is necessary to know the specific heats of sulphur under its various states, and the heats of transformation of this body in passing from the solid to the liquid state, and from the liquid

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to the gaseous state, lastly from the gaseous state developed towards 448°, in which sulphur has a density treble its theoretical density, to the state in which it resumes its normal density. This calculation cannot be performed solely upon the basis of experimental data, which are partly wanting. We have shown how they can be compensated for, up to a certain point (p. 27). The reader will there find the data for the calculation, of which the results will simply be given here.

4. The theoretical temperature developed by the explosion of nitrogen sulphide may be estimated at 4375°.

5. Let us now estimate the pressures.

Take first the *permanent pressure*, that is, the pressure after cooling, the explosion having taken place in a constant capacity. For a density of charge equal to unity, the pressure at 0° would be 242·6 atm., if the volume occupied by the sulphur were *nil*. But one litre in reality contains 340 c.c. of solid sulphur; the permanent pressure will therefore become 367·6 atm.; or 390 kgm. per square centimetre, admitting Mariotte's law.

If the nitrogen sulphide had exploded in an entirely filled capacity, that is to say in its own volume, one kgm. would occupy only 450 c.c. After explosion, the volume of the solid sulphur being deducted, there would remain 110 c.c. for the nitrogen; which would bring the theoretical pressure to 2205·6 atm., or 2340 kgm. per square centimetre.

In general, one kgm. of this substance enclosed in a capacity of n litres, that is to say, supposing the density of charge to be $\frac{1}{n}$, the permanent pressure per square centimetre will be—

$$\frac{250{\cdot}4 \text{ kgm.}}{n - 0{\cdot}340},$$

a theoretical value which will be the nearer the real one the greater n is.

6. The calculation of the pressures developed at the moment of explosion is more hypothetical; we shall, however, refer to it as a term of comparison (see p. 28). This calculation should be performed on the supposition of the sulphur being gaseous at the time of the explosion. The pressure developed will then be, for a density of charge equal to unity—

$$485{\cdot}2 \text{ atm.} \left(1 + \frac{t}{273}\right).$$

Supposing $t = 4375°$, as has been said above,

$$1 + \frac{t}{273} = 17{\cdot}0,$$

and the above product becomes 8246 atm.; or 8555 kgm. per square centimetre.

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If the nitrogen sulphide exploded in its own volume, we should have 18702 kgm.

More generally for the density of charge $\frac{1}{n}$ we shall have—

$$\frac{8555 \text{ kgm.}}{n}.$$

These are the theoretical figures.

7. The following are the real figures which we have obtained with the apparatus described (p. 21) :—

Density of charge.	Pressures.
0·1	815 kgm.
0·2	1703 „
0·3	2441 „

which gives for a density equal to unity, 8150, 8515, and 8137; mean, 8270; a value only slightly lower than the figure 8555, deduced from theory.

These pressures are nearly the same as those of mercury fulminate. However, nitrogen sulphide is much less sudden in its effects, owing, doubtless, to a certain expansion produced by the successive transformations which the sulphur undergoes in cooling—change of gaseous density, liquefaction, and solidification. Hence it follows that the effects produced by the two substances, regarded as detonators and playing the part of caps, must be very dissimilar.

§ 3. Nitrogen Chloride.

1. Nitrogen chloride is considered to be one of the most dangerous bodies to handle, owing to the facility with which it explodes, by shock, friction, or contact with various bodies.

2. Its equivalent = 120·5 grms.

3. Composition—

Nitrogen	116
Chlorine	884
	1000

4. It is liquid, but may, however, be evaporated in a current of air at the ordinary temperature.

5. Its density is equal to 1·65.

6. Nitrogen chloride is decomposed when heated even below 100°, and is slowly destroyed at the ordinary temperature. It explodes on contact with a great number of bodies.

7. Nitrogen chloride explodes, resolving itself into its elements—

$$NCl_3 = N + Cl_3.$$

It develops in this way 44·64 litres of permanent gases, or 370 litres per kilogramme.

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The quantity of heat liberated in this reaction is considerable, but not well known. Indeed, the experiments of Sainte-Claire, Deville, and Hautefeuille on this point[1] have given two numbers which, calculated with the values actually adopted for the heats of formation of ammonia and its chloride (pp. 237 and 243), vary almost from the single to the double.

8. The *permanent pressure* may, however, be calculated. For a density of charge $\frac{1}{n}$ it would be $\frac{370{\cdot}4 \text{ atm.}}{n}$, or $\frac{382{\cdot}7 \text{ kgm.}}{n}$ per square centimetre, supposing n large enough, in order that the chlorine may not assume the liquid state.

On the contrary, if the chlorine be liquefied, the density of liquid chlorine being 1·33, 1065 grms. of this body will occupy 807 c.c., and hence the pressure developed by the nitrogen, which formed only the fourth of the gaseous volume at the normal pressure, will be $\frac{95{\cdot}7 \text{ kgm.}}{n - 0{\cdot}80}$, a much lower figure than that yielded by nitrogen sulphide.

9. The maximum work which can be developed by nitrogen chloride is considerable, but the actual data tend to show that this work is greatly inferior to that of black powder, when an equal weight of both these substances are exploded in any equal capacity. These are results which seem at first sight to contradict what is known of the terrible phenomena produced by nitrogen chloride. Nitrogen chloride is, in fact, regarded as the type of these shattering substances, which cannot be employed in firearms to effect the same work of projection which powder realises by its progressive expansion.

10. We shall now try to account for these differences.

The principal one must doubtless be attributed to the nature of the products of explosion and the complete absence of every compound capable of dissociation. The pressure and the work result from the heat liberated by the decomposition of the nitrogen chloride. Now, the latter gives rise to elementary bodies which have no tendency to recombine, whatever be the

[1] "Comptes rendus des séances de l'Académie des Sciences," tom. lxix. p. 152. The authors employed two reactions—that of chlorine on ammonium chloride in presence of water, and that of hypochlorous acid on the same salt, and they believed the results which follow from their measurements were concordant. But the values deduced from the data they adopted, putting aside certain errors in calculation, would be 51·7 and 39·3. By reckoning, still with the aid of their measurements but by means of the heats of formation actually received for ammonia, hydrochloric acid, and ammonium chloride, we find: 57·8 and 37·8. The discordance in these results is probably owing to the reactions not taking place entirely according to the formulæ indicated. It would be well to resume these measurements, operating upon pure nitrogen chloride and by the decomposition method, synthesis being here very uncertain.

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temperature and pressure. The initial pressure will therefore at once attain its maximum, and nitrogen chloride at once yield the whole work of which it is capable, whether in dislocating the materials on which it acts, or by crushing them, if they are not sufficiently compact, or, lastly, by communicating to them its energy under the form of movements of projection and rotation.

Moreover, the pressure will decrease very suddenly, as much by the fact of these transformations as by that of the cooling and of the expansion of the gases; and it will decrease without any fresh quantity of heat, gradually reproduced, intervening to moderate the rapid fall in pressure. An enormous initial pressure, becoming almost suddenly lowered, are conditions eminently favourable to the rupture of vessels containing nitrogen chloride.

These conditions contrast with those which accompany the combustion of powder, as in the latter the final state of combination of the elements is not produced at the very first in a complete manner, but becomes more advanced according as the temperature falls. The initial pressure could therefore be less with powder than with nitrogen chloride. But, to compensate this, it decreases less quickly, owing to the intervention of the fresh quantities of heat produced during the period of cooling. These considerations have already been insisted upon (p. 12).

In order to fully explain the differences observed between the properties of nitrogen chloride and those of ordinary powder, the duration of the molecular reactions must also be taken into account.

The almost instantaneous transformation of nitrogen chloride develops pressure of which the sudden increase does not give the surrounding bodies time to put themselves into motion, and thus gradually yield to these pressures. It is well known that a film of water on the surface of nitrogen chloride is sufficient to produce such effects.

11. This would be the proper place to speak of nitrogen iodide, a compound so sensitive to shock and to friction that it is hardly possible to isolate it. Everybody has seen the experiments of which this body is the subject in public lectures. But it is so unstable that up to the present it has not been possible to determine its composition with certainty. No attempt has been made to measure its heat of formation.

§ 4. Potassium Chlorate: ClO_3K.

1. Potassium chlorate is not explosive by simple shock or friction at the ordinary temperature. However, the powdered salt, wrapped in a thin piece of platinum foil and strongly struck with a hammer on an anvil, yields some chloride; that is to say, it undergoes partial decomposition.

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When melted and heated too suddenly, it is decomposed with incandescence, and sometimes causes dangerous explosions.

2. The equivalent of potassium chlorate is 122·6.

3. Composition—

Oxygen	...	...	...	392	
Potassium	...	...	...	319	608
Chlorine	...	...	...	289	
				1000	

4. Density, 2·33.

5. Heat of formation—

$$Cl + O_3 + K = ClO_3K \text{ liberates } + 94 \text{ Cal.}$$

6. The salt melts at 334°, without undergoing decomposition, at least if the operation is carried on at constant temperature. It decomposes slowly at 352°, but more rapidly if the temperature be suddenly raised.

This decomposition is effected by two distinct processes.

The salt heated with precaution yields a large quantity of potassium perchlorate—

$$4ClO_3K = KCl + 3ClO_4K,$$

a reaction which liberates + 51·5 Cal., but which would give rise to no gas if it were developed alone.

As a matter of fact, it is always accompanied by another transformation, effected on a considerable portion of matter, viz. the direct decomposition of potassium chlorate into potassium chloride and oxygen—

$$ClO_3K = KCl + O_3.$$

The latter reaction becomes more and more predominant, according as the operation takes place at a higher temperature, or as the substances are superheated. It even seems to be the only one that takes place in presence of copper oxide or of manganese dioxide.

7. This decomposition, referred to the ordinary temperature, liberates + 11 Cal. at constant pressure, or + 11·8 at constant volume.

This makes per kilogramme, 81·6 Cal. at constant pressure and 87·4 Cal. at constant volume.

At 350° and upwards, this reaction liberates more heat, the potassium chlorate being melted, but the exact figure cannot be given, the melting heat of the salt not having been measured.

8. We thus obtain 33·48 litres of gas (reduced volume), or, per kilogramme, 273·1 litres at the normal pressure and at 0°.

9. The molecular specific heat of potassium chloride being 12·9 and the special molecular heat of oxygen, O_3, at constant volume, 7·4, this makes in all 20·3. From this we conclude

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that if these data remained constant, the theoretical temperature of the products would be 581° at constant volume.

The initial body being taken at t, the theoretical temperature would be $581° + t$. Take, for instance, $t = 400°$, the temperature developed by the decomposition would reach 982°. It would even then be increased by some hundred degrees, on account of the heat of fusion of potassium chlorate.

None of these theoretical data are too much at variance with observable results, if the incandescence developed at the moment of the explosive decomposition of potassium chlorate be taken into account.

10. The permanent pressure, after cooling, is calculated, deducting the volume of the potassium chloride, or 304 c.c. per kilogramme of the fixed capacity, in which decomposition took place. For a density of charge $\frac{1}{n}$, we have—

$$\frac{273{\cdot}1 \text{ atm.}}{n - 0{\cdot}304},$$

or, which is the same thing—

$$\frac{282{\cdot}2 \text{ kgm.}}{n - 0{\cdot}304}$$

which makes for $n = 1$: 405 kgm. per square centimetre.

If the chlorate be supposed to explode in its own volume, $n = \frac{1}{2{\cdot}33} = 0{\cdot}429$, that is, the permanent pressure would be 2306 kgm.

11. At the temperature of decomposition, the latter being supposed produced without the aid of an external heating, the theoretical pressure is nearly trebled. It becomes, in fact, neglecting the dilation of the potassium chloride—

$$\frac{273{\cdot}1\left(1 + \frac{t}{273}\right)}{n - 0{\cdot}304} = \frac{855 \text{ atm.}}{n - 0{\cdot}304} = \frac{869 \text{ kgm.}}{n - 0{\cdot}304}$$

per square centimetre.

This makes for $n = 1$: 1248 kgm.

§ 5. Ammonium Nitrite: NH_3HNO_2.

1. The equivalent is equal to 64 grms.
2. The following is the composition :—

Nitrogen	...	...	...	437·5	
Hydrogen	...	...	...	62·5	Water 562·5
Oxygen	...	...	...	500·0	
				1000·0	

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The density is not known.

3. The dry salt may explode when suddenly heated, even below 80°.

4. It is decomposed principally into water and nitrogen, $NO_2HNH_3 = N_2 + 2H_2O$, which yields 22·32 litres of permanent gases, or, for 1 kgm., 349 litres.

5. The same reaction liberates + 73·2 Cal. at constant pressure and + 73·4 Cal. at constant volume, or, for 1 kgm., 1144 Cal. at constant pressure, 1153 Cal. at constant volume.

6. At the temperature of the explosion the water is gaseous, which trebles the volume of the gases. The latter therefore occupy

$$66{\cdot}96 \text{ litres} \left(1 + \frac{t}{273}\right).$$

On the other hand, the heat developed must be referred to the formation of gaseous water, which reduces it to + 53·8 Cal.

7. The theoretical temperature of the products is obtained by dividing 53,800 by 19·2, which gives 2800.

8. The permanent pressure is obtained by subtracting from the fixed capacity the volume of the water, or 562 c.c. for 1 kgm.

For the density of charge, $\frac{1}{n}$, it will therefore be—

$$\frac{349 \text{ atm.}}{n - 0{\cdot}5625} \text{ or } \frac{361 \text{ kgm.}}{n - 0{\cdot}56}$$

for $n = 1$: 820 kgm. per square centimetre.

9. At the theoretical temperature of decomposition the pressure becomes, the water being gaseous—

$$\frac{1147\left(1 + \frac{t}{273}\right)}{n} = \frac{12961 \text{ atm.}}{n} \text{ or } \frac{13393 \text{ kgm.}}{n},$$

which makes for $n = 1$: 13,393 kgm. per square centimetre.

§ 6. Ammonium Nitrate: NO_3HNH_3.

1. Equivalent = 80 grms.

2. Composition—

Nitrogen	350		
Hydrogen	50	Water ...	450
Oxygen	600	Excess of oxygen	200
	1000		

3. Density, 1·707.

4. Heat of formation from the elements—

$$N_2 + H_4 + O_3 = NO_3HNH_3 + 87{\cdot}9 \text{ Cal.}$$

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5. This salt commences to decompose a little above 100°, not without being partly sublimed (p. 243). Towards 200°, it separates in a sufficiently definite manner into nitrogen monoxide and water, without, however, there being a fixed temperature at which this destruction takes place.

If the salt be superheated, and especially from 230° upwards, the decomposition grows more and more rapid (*nitrum flammans*) and ends by becoming explosive at the same time as the salt becomes incandescent (p. 6).

6. A sudden decomposition yields at the same time as nitrogen monoxide various products corresponding to simultaneous decompositions, so that ammonium nitrate can undergo eight distinct transformations, several of which are simultaneous in certain explosive decompositions. We proceed to enumerate them, calculating for each of them the heat developed, the permanent pressure, the theoretical temperature and pressure.

7.—(1st) The integral volatilisation absorbs an unknown quantity of heat, and therefore affords no opportunity for calculation.

8.—(2nd) The integral dissociation into acid and base,

NO_3HNH_3(solid) = NO_3H(gas) + NH_3(gas), would absorb − 41·3;
The fused salt, − 37·3.

This makes, for one kgm. of solid salt, 516 Cal. Hence this reaction is not explosive and cannot be produced without foreign energy.

9.—(3rd) The formation of nitrogen and free oxygen—

$$NO_3HNH_3 \text{ (solid)} = N_2 + O + 2H_2O,$$

would, on the contrary, liberate heat, viz. at constant pressure.

The water being liquid, + 50·1 Cal.; the water being gaseous, + 30·7; at constant volume these figures become + 50·9 and + 33·7. There is, therefore, produced, at the temperature t, a gaseous volume equal to

$$33{\cdot}5 \text{ litres } \left(1 + \frac{t}{273}\right), \text{ the water being liquid;}$$

$$\text{or } 78{\cdot}1 \text{ litres } \left(1 + \frac{t}{273}\right), \text{ the water being gaseous.}$$

$$\text{Or for 1 kgm., } 418{\cdot}7 \text{ litres } \left(1 + \frac{t}{273}\right), \text{ the water being liquid;}$$

$$\text{or } 976 \text{ litres } \left(1 + \frac{t}{273}\right), \text{ the water being gaseous.}$$

The theoretical temperature developed at constant volume would be—

$$\frac{32700}{21.6} = 1501°.$$

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The permanent pressure at 0°, taking into account the volume of the liquid water (450 c.c. for 1 kgm.), will be, for a density of charge $\frac{1}{n}$ —

$$\frac{418{\cdot}7 \text{ atm.}}{n - 0{\cdot}450} \text{ or } \frac{432 \text{ kgm.}}{n - 0{\cdot}450}.$$

For $n = 1$, we should have in theory 787 kgm. per square centimetre. The salt being decomposed in its own volume, that is, 1 grm. occupying 0·585 c.c., the permanent pressure becomes 3200 kgm.

At the temperature developed by decomposition, the water being gaseous, the theoretical pressure would be—

$$\frac{976\left(1 + \frac{1501}{273}\right)}{n} = \frac{6344 \text{ atm.}}{n} \text{ or } \frac{6555 \text{ kgm.}}{n}$$

The salt being decomposed in the same volume which it occupies in the solid state, 11,200 kgm.

These values represent the maximum of the effects which can be produced by the decomposition of ammonium nitrate, all the following reactions producing less heat and a less volume of gas.

10.—(4th) The formation of nitrogen monoxide is the preponderating reaction when we proceed by progressive heating. This reaction,

$$NO_3HNH_3 \text{ (solid) } N_2O + 2H_2O,$$

would liberate—

Liquid water, + 29·5 Cal. at constant pressure, + 30·1 at constant volume.

Gaseous water, + 10·2 Cal. at constant pressure, + 12·1 at constant volume.

The volume of the gases produced at the temperature t will be—

$$22{\cdot}3 \text{ litres} \left(1 + \frac{t}{273}\right), \text{ the water being liquid,}$$

$$66{\cdot}9 \text{ litres} \left(1 + \frac{t}{273}\right), \text{ the water being gaseous;}$$

or for 1 kgm.—

$$278{\cdot}7 \text{ litres} \left(1 + \frac{t}{273}\right), \text{ the water being liquid,}$$

$$836{\cdot}2 \text{ litres} \left(1 + \frac{t}{273}\right), \text{ the water being gaseous.}$$

The theoretical temperature at constant volume is—

$$\frac{12000}{21{\cdot}6} = 555°.$$

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The permanent pressure, at 0°—

$$\frac{278{\cdot}7 \text{ atm.}}{n - 0{\cdot}45} \text{ or } \frac{288 \text{ kgm.}}{n - 0{\cdot}450};$$

but this value is only applicable when n is large enough for the nitrogen monoxide not to be liquefied. For high densities of charge it becomes imaginary.

At the theoretical temperature, the water being gaseous, the pressure would be—

$$\frac{836{\cdot}2\left(1 + \frac{555}{273}\right)}{n} = \frac{2559 \text{ atm.}}{n} \text{ or } \frac{2642 \text{ kgm.}}{n}.$$

The salt being decomposed in the volume which it occupies in the solid state, 4500 kgm. All these values hardly amount to more than the third of the figures corresponding to the formation of free nitrogen.

11.—(5th) The formation of nitric oxide,

$$NO_2HNH_3 \text{ (solid)} = N + NO + 2H_2O,$$

would liberate—

Liquid water, + 28·2 Cal. at constant pressure, + 29·3 at constant volume.

Gaseous water, + 9·2 Cal. at constant pressure, + 11·2 at constant volume.

The volume of the gases produced at the temperature t—

$$33{\cdot}5 \text{ litres} \left(1 + \frac{t}{273}\right), \text{ the water being liquid;}$$

$$78{\cdot}1 \text{ litres} \left(1 + \frac{t}{273}\right), \text{ the water being gaseous.}$$

This volume is the same as in the case of the formation of free nitrogen.

The theoretical temperature at constant volume, $\frac{11200}{21{\cdot}6} = 518°$.

The permanent pressure at 0° is the same as for the formation of free nitrogen, viz. $\frac{432 \text{ kgm.}}{n - 0{\cdot}450}$; it is, moreover, imaginary for high densities of charge, nitric oxide becoming liquefied.

At the theoretical temperature, the water being gaseous, the pressure would be—

$$\frac{976\left(1 + \frac{518}{273}\right)}{n} = \frac{2753 \text{ atm.}}{n} \text{ or } \frac{2840 \text{ kgm.}}{n}.$$

The salt decomposed in the volume which it occupies in the

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solid state, 4860 kgm.; values nearly the same as those corresponding to nitrogen monoxide.

12.—(6th) The formation of nitrogen trioxide—

$$3NO_3H, NH_3 \text{ (solid)} = 4N + N_2O_3 + 6H_2O.$$

Liquid water, + 42·5 Cal. at constant pressure, + 43·1 at constant volume.

Gaseous water, + 23·3 Cal. at constant pressure, + 25·1 at constant volume.

The volume of the gases at the temperature t is the same as for nitrogen monoxide, viz.—

$$+ 22{\cdot}3 \text{ litres } \left(1 + \frac{t}{273}\right), \text{ the water supposed liquid;}$$

$$+ 66{\cdot}9 \text{ litres } \left(1 + \frac{t}{273}\right), \text{ the water supposed gaseous.}$$

In all cases this reaction can only be developed upon a fraction of matter; nitrogen trioxide existing only in the dissociated state in presence of nitric oxide and nitric peroxide, which are in excess. Hence it appears useless to give the calculations relative to the pressures and temperatures, a remark which is equally applicable to the following reactions.

(7th) The formation of nitric peroxide,

$$2NO_3HNH_3 \text{ (solid)} = N_3 + NO_2 + 4H_2O,$$

would liberate—

Liquid water, + 48 Cal. at constant pressure, + 49·5 at constant volume.

Gaseous water, + 29·5 Cal. at constant pressure, + 31·4 at constant volume.

The volume of the gases, at the temperature t, is the same as for nitrogen monoxide and for nitrogen trioxide.

(8th) The formation of gaseous nitric acid,

$$5NO_3HNH_3 \text{ (solid)} = 2HNO_3 + 8N + 9H_2O,$$

would liberate, the acid and the water being gaseous, and not combined, + 33·4 Cal. at constant pressure, + 35·1 Cal. at constant volume.

The volume of the gases at the temperature t, the water and the acid assuming the gaseous state, would be 67 litres $\left(1 + \frac{t}{273}\right)$. That of the permanent gases, 17·8 litres $\left(1 + \frac{t}{273}\right)$, being the least of all. On the contrary, the heat liberated is the greatest. But this mode of decomposition is accessory.

13. We have deemed it useful to develop the study of the manifold and simultaneous modes of decomposition of am-

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monium nitrate, as typical in the study of explosive substances; this multiplicity of simple reactions not being known, generally speaking, with precision, for the other bodies. It will be noticed with regard to this point that in the explosive decompositions of this salt, the heat at constant volume may vary from + 35·1 Cal. to 11·2 Cal.; the volume of the gases, from 62·5 litres $\left(1 + \frac{t}{273}\right)$ to 78·1 litres $\left(1 + \frac{t}{273}\right)$.

§ 7. Ammonium Perchlorate: ClO_4H, NH_3.

1. Equivalent, 117·5.
2. Composition—

Cl	... ...	= 302
N	... ...	= 119
H	... ...	= 34
O	... ...	= 545
		1000

3. Heat of formation from the elements—

$$Cl + N + H_4 + O_4 = ClO_4H, NH_3 + 79·7.$$

4. The decomposition of this salt by heat has already been studied (p. 356). The principal reaction is ClO_4H, NH_3 (solid) $= Cl + O_2 + N + 2H_2O$ (gaseous) + 38·3 Cal.; the water being liquid, + 58; or, for 1 kgm., 4963 Cal.

At constant volume we should have, + 59·5 Cal., the water being liquid, and + 40·7, the water being gaseous.

5. This reaction produces at the temperature t, the water being supposed liquid, 44·6 litres $\left(1 + \frac{t}{273}\right)$; the water gaseous, 89·3 litres $\left(1 + \frac{t}{273}\right)$; or, for one kgm., 379·6 litres $\left(1 + \frac{t}{273}\right)$, the water being liquid, and 759·2 litres $\left(1 + \frac{t}{273}\right)$, the water gaseous.

6. Theoretical temperature at constant volume,

$$\frac{40700}{24·9} = 1563°.$$

7. The permanent pressure at 0°, for a density of charge $\frac{1}{n}$, taking into account the volume of the liquid water (307 c.c. for 1 kgm.), would be—

$$\frac{379·6 \text{ atm.}}{n - 0·307} \text{ or } \frac{392 \text{ kgm.}}{n - 0·307}.$$

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But this figure is only applicable to low densities of charge. For high densities the chlorine is liquefied and occupies 227 c.c. The volume of the permanent gases is in this way diminished by one-fourth.

The permanent pressure then becomes $\frac{294 \text{ kgm.}}{n - 0{\cdot}534}$, which makes, for $n = 1$, 631 kgm. per square centimetre.

At the theoretical temperature of decomposition, the water and the chlorine being gaseous, the pressure becomes—

$$\frac{893 \text{ atm.}\left(1 + \frac{1563}{273}\right)}{n} = \frac{6004 \text{ atm.}}{n} \text{ or } \frac{6204 \text{ kgm.}}{n},$$

figures which are not very remote from the maximum effects of which ammonium nitrate is capable.

The decomposition which served as base for the foregoing calculations is not exclusive, a small quantity of perchlorate being decomposed at the same time with formation of hydrochloric acid; now

$2ClO_4NH_3 = 2HCl + 3H_2O + N + O_5$ liberates + 30·8 Cal.,

producing 100·4 litres $\left(1 + \frac{t}{273}\right)$ of gas. But this reaction is accessory.

§ 8. Ammonium Bichromate: $Cr_2O_6\ (NH_4)_2O$.

1. We shall take this salt as a type of the ammoniacal salts formed by the metallic oxacides.

Its equivalent is 126·4.

2. Composition—

N	...	...	...	...	...	=	111
Cr	...	...	...	...	...	=	415
H	...	...	...	...	...	=	32
O	...	...	...	...	...	=	442
							1000

3. The heat of formation from the elements cannot be calculated, the heat of oxidation of chromium being unknown. But the decomposition of the salt not producing any oxide lower than the chromium sesquioxide, it is sufficient to calculate its formation from this oxide and the pre-existing water contained in salts of ammonia.

The author has thus found:[1]

$$Cr_2O_3 \text{ (precip.)} + O_4 + H_8 + N_2 = Cr_2O_3 + 2NH_3 + H_2O \text{ (solid)} + 79{\cdot}0 \text{ Cal.}$$

[1] "Comptes rendus des séances de l'Académie des Sciences," tom. xcvi. pp. 399 and 536.

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Cr_2O_3 (precip.) + H_2O (liquid) + O_3 + H_6 + N_2 = Cr_2O_6, $(NH_4)_2O$ (solid) liberates + 44·5.

Cr_2O_3 (precip.) + O_3 + $2H_3N$ (dissolved) + H_2O (liquid) = Cr_2O_6, $(NH_4)_2O$ = solid + 23·5; dissolved + 17·3.

Some remarks are here necessary.

The above figures are relative to a special state of chromium oxide, namely when precipitated cold from dilute chrome alum, by dilute potash, used in strictly equivalent quantity. But they vary according to the manifold states of this oxide;[1] the variation by the precipitated oxide may amount to as much as + 6·9 Cal. according to the author's observations. With the anhydrous oxide, and especially with the state produced by ignition,[2] the difference would be even greater, a circumstance which explains the greater resistance to the acids of calcined chromium oxide. In the case of the formation of the chromates the heat liberated must be diminished by the heat of transformation of the ordinary chromium oxide into calcined oxide, say for example $-q$. This quantity is, on the contrary, added to the heat liberated by the explosive decompositions in which the chromates intervene.

4. Ammonium bichromate, briskly heated, becomes incandescent and is tumultuously decomposed with formation of water and chromium oxide in virtue of a real internal combustion—

$$Cr_2O_6(NH_4)_2O = Cr_2O_3 + 4H_2O + N_2.$$

This reaction liberates—

The water liquid, + 59 Cal. at constant pressure, + 60·4 Cal. at constant volume.

The water gaseous, 39·0 Cal. + q at constant pressure, + 40·4 Cal. at constant volume.

The direct reaction of chromic acid on ammonia gas, in the absence of water, would liberate nearly the double

C_2O_6 (solid) + $2NH_3$ (gas) = Cr_2O_3 + N_2 + $3H_2O$ (gas) + 73·3 Cal. + q at constant pressure.

5. The explosive decomposition of ammonium bichromate produces the following gaseous volumes:—

$$\text{The water liquid, } 11{\cdot}2 \text{ litres } \left(1 + \frac{t}{273}\right);$$

$$\text{The water gaseous, } 55{\cdot}7 \text{ litres } \left(1 + \frac{t}{273}\right).$$

[1] "Comptes rendus des séances de l'Académie des Sciences," tom. xcvi. p. 87.
[2] Berzelius.

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Or for 1 kgm.—

$$88{\cdot}6 \text{ litres } \left(1 + \frac{t}{273}\right), \text{ the water liquid;}$$

$$44{\cdot}3 \text{ litres } \left(1 + \frac{t}{273}\right), \text{ the water gaseous.}$$

6. Theoretical temperature, at constant volume (the chromium oxide solid), $+ \frac{40400}{31{\cdot}1} = 1300°$, or, more accurately, $1300° - \frac{q}{31{\cdot}1}$.

7. Permanent pressure at 0°, taking into account the volume of the liquid water and of the chromium oxide (density + 5·2)—

$$\frac{88{\cdot}6 \text{ atm.}}{n - 0{\cdot}401} \text{ or } \frac{91{\cdot}6 \text{ kgm.}}{n - 0{\cdot}401}.$$

For $n = 1$, we have 153 kgm. per square centimetre, a much lower pressure than that of the foregoing bodies.

At a high temperature, the vaporisation of the water tends to increase fivefold the pressure which would be attributable to nitrogen alone.

Hence, at the theoretical temperature of the decomposition, we should have the pressure[1]—

$$\frac{443 \text{ atm.} \left(1 + \frac{1300}{273}\right)}{n - 0{\cdot}116} = \frac{2570 \text{ atm.}}{n - 0{\cdot}116} \text{ or } \frac{2656 \text{ kgm.}}{n - 0{\cdot}116}.$$

For $n = 1$, this figure is increased to about 2990 kgm.

All these values are much lower than those relative to the foregoing bodies; that is, ammonium nitrate and perchlorate.

[1] Neglecting the quantity q.

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CHAPTER V.

NITRIC ETHERS PROPERLY SO CALLED.

§ 1.

We shall describe the following ethers regarded as types of the nitric derivatives of monatomic and polyatomic alcohols:—

Nitric ether of ordinary alcohol, of which the author has measured the heat of formation.

Nitro-methylic ether, employed lately in dyeing.

Dinitric ether of glycol, remarkable because its decomposition corresponds to a total combustion without an excess of any element.

Trinitric ether of glycerin or nitroglycerin.

Lastly, hexanitric ether of mannite, or nitromannite.

It would be advisable to add to these, for the sake of completeness, the explosive mixtures formed by the association of an organic compound with fuming nitric acid, or with nitric peroxide, but these mixtures are elsewhere studied.

§ 2. Nitro-ethylic Ether: $C_2H_4(HNO_3)$.

1. Equivalent, 91.
2. Composition—

C	... ...	= 264
H	... ...	= 55
N	... ...	= 154
O	... ...	= 527
		1000

3. The body is liquid, boiling at 86°.
4. Density: 1·132 at 0°.
5. This ether can be inflamed when a small quantity of the liquid is operated upon. In this way nitrous vapour is formed in abundance, but if the vapour of the ether be superheated beforehand, it explodes violently.

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6. The heat of formation from the elements has been found (p. 279)—

$$C_2\,(\text{diamond}) + H_5 + N + O_3 = C_2H_4(NO_3H)\,(\text{liquid}) + 49{\cdot}3\ \text{Cal.}$$

In the gaseous state it should be nearly + 42 Cal.

The heat of total combustion of the liquid body by an excess of oxygen, + 311·2 Cal.

7. The following decomposition,

$$C_2H_4(NO_3H) = 2CO + H_2O + 3H + N,$$

would liberate, the ether and water being liquid, + 71·3 Cal. at constant pressure, + 73·5 Cal. at constant volume. All the bodies being supposed gaseous, the heat liberated must have nearly the same value.

Lastly, the ether being liquid and the water gaseous, we should have, + 61·3 Cal. at constant pressure, + 64·6 Cal. at constant volume.

For 1 kgm. we should have at constant pressure, the ether and the water being liquid, 783·5 Cal.; at constant volume, 791·6 Cal.

We shall not here examine the other possible modes of decomposition.

8. The volume of the permanent gases, at the temperature t, will be, for 1 equiv. = 91 grms.—

89·3 litres $\left(1 + \frac{t}{273}\right)$, the water being gaseous, 111·6 litres $\left(1 + \frac{t}{273}\right)$; or, for 1 kgm., 981·3 litres $\left(1 + \frac{t}{273}\right)$, for the permanent gases, 1226 litres $\left(1 + \frac{t}{273}\right)$ if gaseous water be added.

9. The theoretical temperature, at constant volume—

$$\frac{64000}{26{\cdot}4} = 2424°.$$

10. The permanent pressure, at 0° (the liquid water occupying 198 c.c.)—

$$\frac{981\ \text{atm.}}{n = 0{\cdot}198} \text{ or } \frac{1016\ \text{kgm.}}{n - 0{\cdot}198}.$$

But this formula is only applicable to low densities of charge, owing to the liquefaction of carbonic acid produced at high densities.

11. The pressure developed at the theoretical temperature and calculated according to the laws of gases—

$$\frac{1226\ \text{atm.}\left(1 + \frac{2425}{273}\right)}{n} = \frac{12137\ \text{atm.}}{n} \text{ or } \frac{12541\ \text{kgm.}}{n}.$$

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§ 3. Nitro-methylic Ether: $CH_2(NO_3H)$.

1. Equivalent, 77.
2. Composition—

C	...	...	...	...	...	= 156
H	...	...	...	...	...	= 39
N	...	...	...	...	...	= 182
O	...	...	...	...	...	= 623
						1000

3. This body is liquid, boiling at 66°.
4. Density at 20°: 1·182.
5. This ether can be inflamed in small quantities at the ordinary temperature, but its vapour, superheated to about 150°, explodes violently. It may even explode cold, on contact with a flame,[1] and communicate the explosion to liquid ether.
6. Heat of formation from the elements (p. 284)—

$$C\,(\text{diamond}) + H_2 + N + O_3 = CH_2(NO_3H)\,(\text{liquid}) + 39{\cdot}6\ \text{Cal.}$$

7. The ether being gaseous, this figure must be nearly + 32. The heat of total combustion of the liquid body, + 157·9.
8. Admitting the following decomposition—

$$2CH_2(NO_3H) = CO_2 + CO + 3H_2O + N_2,$$

the heat liberated at constant pressure would be, the ether being liquid, the water gaseous, + 113 Cal. at constant pressure, + 114 Cal. at constant volume; the ether and water being both liquid, + 123·8 Cal., or for 1 kgm. 1605.

All the other bodies being gaseous the heat liberated remains nearly the same.

9. The volume of the permanent gases for 1 equiv., 33·5 litres $\left(1 + \frac{t}{273}\right)$, for the water gaseous 66·9 litres $\left(1 + \frac{t}{273}\right)$; or, for 1 kgm., for the permanent gases 435 litres $\left(1 + \frac{t}{273}\right)$, when the water is gaseous 869 litres $\left(1 + \frac{t}{273}\right)$.

10. Theoretical temperature at constant volume—

$$\frac{114900}{19{\cdot}2} = 5984°.$$

11. Permanent pressure, at 0° (the liquid water occupying 351 c.c.)—

$$\frac{435\ \text{atm.}}{n - 0{\cdot}351} \text{ or } \frac{448\ \text{kgm.}}{n - 0{\cdot}351}.$$

This value is applicable only to low densities of charge, that

[1] Explosion at Saint-Denis, November 19, 1874.

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is to say, within the limits in which carbonic acid retains the gaseous state.

12. Pressure at the theoretical temperature, calculated according to the laws of gases—

$$\frac{669 \text{ atm.} \left(1 + \frac{5984}{273}\right)}{n} = \frac{15052 \text{ atm.}}{n},$$

or 15,534 kgm. per square centimetre.

The permanent pressures are much lower than for nitroethylic ether, but the heat liberated is more than double, which gives an advantage to the theoretical pressure.

§ 4. Dinitro-glycolic Ether: $C_2H_2(NO_3H)_2$.

1. Equivalent, 152.
2. Composition—

C	...	...	...	...	...	= 158
H	...	...	...	...	...	= 26
N	...	...	...	...	...	= 184
O	...	...	...	...	...	= 632
						1000

This composition is very nearly the same as that of nitromethylic ether.

3. The body is liquid.

4. The heat of formation from the elements calculated from the formula on p. 285—

C_2 (diamond) + H_4 + N_2 + O_6 = $C_2H_2(HNO_3)_2$ (liquid) + 66·9 Cal.

5. The heat of total combustion and the heat of explosive decomposition coincide—

$$C_2H_2(NO_3H)_2 = 2CO_2 + 2H_2O + N_2 + 259{\cdot}1 \text{ Cal.}$$

at constant pressure, the water being liquid; + 260·7 Cal. at constant volume.

For 1 kgm. we shall have 1705 Cal. at constant pressure, 1715 Cal. at constant volume.

6. Volume of the permanent gases for 1 equiv., 86·9 litres $\left(1 + \frac{t}{273}\right)$, the water being gaseous 111·6 litres $\left(1 + \frac{t}{273}\right)$; or, for 1 kgm., 440 litres $\left(1 + \frac{t}{273}\right)$ for the permanent gases, 734 litres $\left(1 + \frac{t}{273}\right)$ when the water is gaseous.

7. Theoretical temperature—

$$\frac{241{,}900}{33{\cdot}6} = 7982°.$$

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8. Permanent pressure, at 0° (the liquid water occupies 237 c.c.)—

$$\frac{440 \text{ atm.}}{n - 0{\cdot}237} \text{ or } \frac{455 \text{ kgm.}}{n - 0{\cdot}237},$$

a value only applicable to low densities of charge.

9. Pressure at the theoretical temperature calculated according to the laws of gases—

$$\frac{734\left(1 + \frac{7982}{273}\right)}{n} = \frac{22170 \text{ atm.}}{n},$$

or 22,910 kgm. per square centimetre.

§ 5. Nitroglycerin: $C_3H_2(NO_3H)_3$.

1. Nitroglycerin is considered the most powerful of explosive substances. In spite of terrible accidents, its extraordinary properties have been taken advantage of for industrial purposes. The manufacture of nitroglycerin in France commenced on a large scale during the siege of Paris, at the instance and under the direction of the Scientific Committee of Defence. Since then it has assumed an ever-increasing importance, dynamite tending to replace blasting powder in the greater number of its uses.

It is not our intention to make here a complete study of nitroglycerin and dynamites, nor of their industrial or military applications; but it enters into the scope of the present work to present the figures which express the heat and pressure developed by the explosive decomposition of nitroglycerin.

We shall, therefore, devote a paragraph to pure nitroglycerin, reserving the study of dynamites for the following chapter.

2. Formula: $C_3H_2(NO_3H)_3$.

Equivalent, 227.

3. Composition—

C	...	...	...	...	...	= 159
H	...	...	...	...	...	= 22
N	...	...	...	...	...	= 185
O	...	...	...	...	...	= 634
						1000

4. Nitroglycerin is liquid, but solidifies at + 12°. These circumstances play an important part in the properties of dynamite.

The density of liquid nitroglycerin is 1·60.

This body is very soluble in alcohol or ether, but only very slightly soluble in water. Nevertheless, in presence of a sufficient quantity of water, it is entirely dissolved, which does

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not permit of allowing nitroglycerin, either free or associated with a pulverulent substance, to remain long in a current of water.

It is poisonous.[1]

5. Nitroglycerin is very sensitive to shock, and explodes easily by the shock of iron on iron or silicious stone. The fall of a flask or of a stone jar has occasionally sufficed to cause explosion. The shock of copper on copper, and especially of wood on wood, is considered less dangerous; however, there are instances of explosion provoked by a shock of this kind.

6. Pure nitroglycerin keeps for an indefinite time. The author has kept a bottle of it in his collections for ten years without it showing any signs of alteration. But a little moisture, or a trace of free acid, is sufficient to excite a decomposition, which, when once commenced, is sometimes accelerated up to the point of inflammation, and even of explosion of the substance.

The action of solar light also causes the decomposition of nitroglycerin, as well as that of the nitric compounds in general.

Electric sparks inflame it, though with difficulty. They may even cause it to explode under certain conditions; for instance, under the influence of a series of strong sparks, nitroglycerin changes, turns brown, then explodes.

Submitted to the action of heat, it is volatilised to an appreciable extent, especially towards 100°; it may even be completely distilled, if this temperature be long maintained. But if the temperature be suddenly raised to about 200°, nitroglycerin ignites; and a little above it, explodes with terrible violence.

Its inflammation, caused by contact with an ignited body, gives rise to nitrous vapour and a complex reaction, with the production of a yellow flame, without explosion, properly so called, at least as long as small quantities of matter are operated upon. But if the mass be too great it ends by exploding.

The explosion of nitroglycerin corresponds to a very simple decomposition—

$$2C_3H_2(NO_3H)_3 = 6CO_2 + 5H_2O + 6N + O.$$

It will be seen that nitroglycerin possesses the exceptional property of containing more oxygen than is necessary for completely burning its elements.

7. Heat of formation from the elements (p. 282)—

$$C_3 \text{ (diamond)} + H_3 + N_3 + O_9 = C_3H_2(NO_3H)_3 \text{ liberates } + 98 \text{ Cal.}$$

8. The heat of total combustion and the heat of decomposi-

[1] For the preparation with the aid of two binary mixtures made beforehand, see Boutmy et Faucher, "Comptes rendus des séances de l'Académie des Sciences," tom. lxxxiii. p. 786.

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tion are identical, according to what has just been said. The reaction will, therefore, be represented by the following formula :—

$$2C_3H_2(NO_3H)_3 = 6CO_2 + 5H_2O + 6N + O.$$

The heat developed will be—

The water being liquid, at constant pressure + 356·5 Cal., at constant volume + 358·5 Cal.

The water being gaseous, at constant pressure + 331·1 Cal., at constant volume + 335·6 Cal.

For 1 kgm., at constant pressure, the water being liquid, 1570 Cal.; at constant volume, 1579 Cal.

Sarrau and Vieille found 1600, a figure the difference between which and the above does not exceed that which might be due to experimental errors.

In the miss-fires, treated of on page 283, the heat liberated is necessarily less, the combustion being incomplete.

9. Volume of the permanent gases for 1 equiv.—

$$106 \text{ litres } \left(1 + \frac{t}{273}\right), \text{ the water being liquid;}$$

$$161{\cdot}8 \text{ litres } \left(1 + \frac{t}{273}\right), \text{ the water being gaseous.}$$

Or, for 1 kgm., 467 litres $\left(1 + \frac{t}{273}\right)$, the water being liquid.

Sarrau and Vieille found 465 litres, at 0°, by experiment.

We should have 713 litres $\left(1 + \frac{t}{273}\right)$, the water being gaseous.

For a litre of liquid nitroglycerin we should have, lastly—

$$747 \text{ litres } \left(1 + \frac{t}{273}\right) \text{ the water being liquid;}$$

$$1141 \text{ litres } \left(1 + \frac{t}{273}\right), \text{ the water being gaseous.}$$

10. Theoretical temperature, at constant volume—

$$\frac{335600}{48} = 6980°.$$

11. Permanent pressure (the liquid water occupies 198 c.c.)—

$$\frac{467 \text{ atm.}}{n - 0{\cdot}198} \text{ or } \frac{482 \text{ kgm.}}{n - 0{\cdot}198}.$$

This figure is only applicable to low densities of charge and with the usual exception as to the liquefaction of carbonic acid.

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12. Pressure at the theoretical temperature—

$$\frac{713\left(1+\frac{6980}{273}\right)}{n} = \frac{18966 \text{ atm.}}{n}, \text{ or } 19{,}580 \text{ kgm. per square centimetre.}$$

13. Let us compare this result with the pressures observed by Sarrau and Vieille by means of the crusher and with dynamite at 75 per cent.

They found under the density of charge—

$\frac{1}{n}$ =	0·2	1420 kgm.	
	0·3	2890 „	
	0·4	4265 (3984 and 4546) kgm.	
	0·5	6724 (6902 and 6546) „	
	0·6	9004 kgm.	

The volume occupied by the silica, after undergoing the temperature of the explosion, may be estimated at 0·1 c.c. for 1 grm. of dynamite. Consequently, the volume occupied by the gas yielded by 1 grm. of pure nitroglycerin would be equal to $\frac{4}{3}(n - 0{\cdot}1)$, neglecting the expansion of silica by heat.

We find in this way, referring the corrected densities of charge to nitroglycerin, and calculating the pressures from the results of the "crushers"—

$$n' = 6{\cdot}5 \text{ c.c. } \frac{P'}{n'} = 9230 \text{ kgm.}$$

4·3 c.c.	12430 kgm.	
3·2 „	13640 „	
2·5 „	16800 „	
2·1 „	18900 „	

It will be noticed that the values of $\frac{P'}{n'}$ are not constant. But here intervenes the new theory of crushing manometers by Sarrau and Vieille (p. 23), which accounts for these variations by the duration of decomposition of dynamite and tends to reduce by one-half the figure obtained with very high densities of charge.

According to their new trials, made with very heavy piston, for the density $\frac{1}{n'} = 0{\cdot}3$, we obtain a pressure of 2413 kgm., which corresponds to $n' = 4{\cdot}3$ c.c.

$$\frac{P'}{n'} = 10{,}376 \text{ kgm.}$$

If we wish to compare with strict accuracy these figures with the theoretical pressures, the heat yielded to the silica must be taken into account in calculating the latter. Let the specific

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heat of silica be supposed constant and equal to 0·19, which makes for 73·7 grms. of silica 14·4, the theoretical temperature becomes—

$$\frac{335600}{62{\cdot}4} = 5378°.$$

The corresponding pressure will be—

$$\frac{713\left(1+\frac{8378}{273}\right)}{n} = \frac{14759 \text{ atm.}}{n} \text{ or } \frac{15281 \text{ kgm.}}{n}.$$

a value higher by a third than the actual figure found for high densities.

14. To sum up—weight for weight nitroglycerin produces three and a half times as much permanent gases reduced to 0° as nitrate powder, and twice as much as chlorate powder.

At equal volumes it produces nearly six times as much permanent gases as ordinary powder. As, moreover, it produces weight for weight more than double the heat, the difference between the effects of the two substances taken in equal weights is easy to foresee.

At equal volumes this difference is still greater. Thus one litre of nitroglycerin weighs 1·60 kgm., whilst one litre of ordinary powder weighs about 0·906 kgm. At the same volume as powder, nitroglycerin will develop a pressure ten or twelve times greater; which may be actually realised in a completely filled capacity, as in the case of a blast-hole, or when operating under water. Under these conditions the maximum work developed by one litre of nitroglycerin may amount to a value treble that of the maximum work of ordinary powder at the same volume. These colossal figures, no doubt, are never attained in practice, especially owing to phenomena of dissociation, but the fact that they are approached is sufficient to explain why the work, and especially the pressures developed by nitroglycerin, exceed the effects produced by all the other explosive substances industrially employed. The relations which these figures show between nitroglycerin and ordinary powder, for example, agree pretty closely with the empirical results observed in the working of mines.[1]

15. The rupture into fragments and the explosion of wrought iron,[2] effects which cannot be produced by ordinary powder,

[1] See the experiments cited in the small treatise "La Dynamite," by Trauzl, extracted by P. Barbe, pp. 91 and 92 (1870). The usual effect of nitroglycerin in quarries has been found to be five or six times greater than that of blasting powder, weight for weight. For an equal volume in blast-holes, there is obtained with dynamite about eight times the effect produced by powder; that is to say, eleven times the same effect for a given weight of pure nitroglycerin employed under this form. This refers to effects of dislocation, which depend especially upon the initial pressures.

[2] Same work (pp. 98 and 99).

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are fresh proofs of the enormous initial pressures developed by nitroglycerin. The question of the rapidity of decomposition, moreover, intervenes here (p. 35).

Although nitroglycerin is shattering, it nevertheless fractures rocks without crushing them into small fragments. The facts observed during the study of the pressures exerted by the crushers, at various densities of charge, would lead us to foresee this property. It may also be accounted for by the phenomena of dissociation. The elements of water and carbonic acid will be partly separated in the first instance, which diminishes the initial pressures; but the formations of water and carbonic acid being completed during expansion, successively reproduce fresh quantities of heat, which regulate the fall of the pressures. Nitroglycerin will therefore act during expansion in a similar manner to ordinary powder. However, the dissociation will be less with nitroglycerin, because the compounds formed are simpler and the initial pressures higher.

In short, nitroglycerin combines the apparently contradictory properties of various explosive substances: it is shattering, like nitrogen chloride; dislocates and fractures rocks without crushing them, like ordinary powder, though with more intensity; lastly, it produces excessively great effects of projection. All these properties, recognised by observers, can be foreseen and explained by theory.

16. It could further be shown that inflammation induced at a point of the mass is less dangerous with nitroglycerin than with chlorate and even nitrate powder, seeing that the combustion of the same weight of matter raises the temperature of the neighbouring parts to a less extent, either owing to the cooling produced by contact with the surrounding liquid parts, or, especially, owing to the specific heat of nitroglycerin, which appears to be much greater than that of potassium chlorate and nitrate powders.

With regard to the theory of the effects of shock on nitroglycerin, the reader is referred to p. 52.

17. Lastly, let us compare nitroglycerin with ordinary powder from the point of view of the best use of a given weight of potassium nitrate. According to the equivalent, 303 parts of nitre produce either 404 parts of ordinary powder, or 227 parts of nitroglycerin, that is to say, a weight less by half. But as a set-off the latter can develop, under the most favourable circumstances, a pressure from eight to ten times greater than the same volume of powder.

It follows from these numbers that a given weight of potassium nitrate, if it could be changed atomically, and without loss, into nitroglycerin, would develop in a blast-hole a pressure treble that yielded by ordinary powder, made with the same weight of nitrate.

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§ 6.—Nitromannite: $C_6H_2(NO_3H)_6$.

1. Equivalent, 452.
2. Composition—

C	...	...	...	...	...	= 159
H	...	...	...	...	...	= 18
N	...	...	...	...	...	= 186
O	...	...	...	...	...	= 637
						1000

The body crystallises in fine white needles. It must be carefully purified by being re-crystallised in alcohol to free it from the products of incomplete nitrification.

3. Its apparent density is 1·60, but by melting it under pressure as much as 1·80 may be observed at 20°.

4. It melts between 112° and 113°, and solidifies at 93°.

The temperature of the melting point given by various authors falls to 70°, but this is for an impure product.

5. Nitromannite commences to give off acid vapours from the melting temperature. But this emission is very slow; it is accelerated with the rise in temperature. When suddenly heated to about 190° it takes fire; towards 225° it deflagrates, towards 310° it explodes.

When the heating has been progressive, and accompanied by a commencement of decomposition, which alters the composition of the residuum, inflammation and explosion can no longer take place.

6. Nitromannite purified by crystallisation in alcohol and kept protected from sunlight can be kept for several years without alteration.

But if care be not taken to re-crystallise it, it contains much more changeable products, which cause its progressive decomposition. These products also lower its melting point to about 70°.

7. Nitromannite explodes by the shock of iron on iron more readily than nitroglycerin, but with rather more difficulty than mercury fulminate. It is intermediate in its shattering properties. It explodes by the shock of copper on iron or copper, and even of porcelain on porcelain, provided the latter shock be violent.

8. The heat of formation of nitromannite from the elements has been found (p. 283), + 156·1 Cal., according to a calculation founded on the heats of formation of mannite, nitric acid, and nitromannite, or + 161·4 according to the heat of combustion observed by Sarrau and Vieille.

9. The heat of total combustion coincides with the heat of decomposition (see p. 283). It is equal to + 683·9 Cal. at con-

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stant pressure, the water being liquid, or 689·6 at constant volume. Or, for 1 kgm., at constant pressure, 2513 Cal.; at constant volume, 1529 Cal.—

$$C_6H_2(NO_3H)_6 = 6CO_2 + 4H_2O + 3N_2 + O_2.$$

Sarrau and Vieille found 1512 at constant volume, and proved, further, that the decomposition really takes place according to the above equation.

The heat of combustion is inferior to that of nitroglycerin and of nitroglycol, an inferiority due to the formation of a larger amount of free oxygen.

10. Volume of the permanent gases for 1 equiv.—

223 litres $\left(1+\frac{t}{273}\right)$; the water being gaseous, $\left(1+\frac{t}{203}\right)$ 312 litres.

The water being gaseous, we should have for 1 equiv. at constant pressure + 603·9 Cal., at constant volume + 612 Cal.

Or, for 1 kgm., 494 litres $\left(1+\frac{t}{273}\right)$ for the permanent gases, 692 litres $\left(1+\frac{t}{273}\right)$ the water being gaseous.

11. Theoretical temperature, $\frac{612000}{91{\cdot}2} = 6710°$.

12. Permanent pressure at 0° (the liquid water occupies 159 c.c.)—

$$\frac{494 \text{ atm.}}{n - 0{\cdot}159} \text{ or } \frac{510 \text{ kgm.,}}{n - 0{\cdot}159}$$

subject to the usual proviso as to the lowness of the densities of charge and of the limit of liquefaction of carbonic acid.

13. Pressure at the theoretical temperature, calculated according to the laws of gases—

$$\frac{692\left(1+\frac{6710}{273}\right)}{n} = \frac{17220 \text{ atm.}}{n} \text{ or } \frac{17760 \text{ kgm.}}{n}$$

or 23,510 kgm. per square centimetre, a value very close to those which belong to nitroglycol (22,910) and nitroglycerin (19,580), as might be expected.

14. The pressures actually exerted in the explosion of nitromannite have been measured by Sarrau and Vieille. These authorities found—

At the density of charge 0·1, 2273 kgm.

At the density of 0·2, 4634 kgm.

Or as mean, $\frac{22950}{n}$, a value very near the theoretical figure.

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But the new theory of the authors would tend to reduce it to the half (p. 23).

But this pressure is so quickly developed that the piston of the crusher is often broken, which shows the shattering character of nitromannite. The same property intervenes in the tests founded on the capacity of chambers hollowed in leaden blocks by various explosives (p. 374). Now, the capacity hollowed by a given weight of nitromannite is greater by a fourth (43 c.c. for 1 grm.) than that hollowed by nitroglycerin (35 c.c. for 1 grm.) Nitromannite, moreover, manifests a much more marked tendency to tear the leaden blocks in diagonal directions. These facts contrast with the theoretical calculation of the pressures or of the maximum work, which give nearly the same value for nitromannite and nitroglycerin. They show that the empirical method of chambers hollowed by an explosive does not really measure either the pressure or the work, but certain more complicated effects.

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CHAPTER VI.

DYNAMITES.[1]

§ 1. Dynamites in General.

1. In 1866, in consequence of terrible accidents caused by explosions,[2] the use of this substance was going to be forbidden everywhere, when a Swede, Mr. Nobel, conceived the idea of rendering it less sensitive to shocks by mixing it with an inert substance, a well-known artifice for attenuating the effects of the ordinary powder, but which leads to unexpected results in the present case. Nobel added to it first a little methylic alcohol; then, this expedient being insufficient, he mixed it with amorphous silica. He designated this mixture by the name of *dynamite*.

He soon recognized, and this was a very important discovery, that the explosion requires the use of special mercury fulminate detonators, and that it acquires in this way an exceptional violence; it can then be produced even under water. By using these detonators tamping may be dispensed with, when absolutely necessary, in blasting with dynamite.

This name has since been extended to very diversified mixtures, with nitroglycerin as base, and at the present day a score of different dynamites are distinguished. Mixtures containing liquid explosives other than nitroglycerin have even been designated by the same word. Dynamites have the common property of not exploding either by simple inflammation, slight shock, or moderate friction. But they explode, on the contrary, by the use of strong caps, called detonators, generally composed of mercury fulminate.

Dynamites are divided into several classes.

2. In some, containing an inert base, the nitroglycerin is

[1] See "La Nitroglycerine et les Dynamites," par Fritsch, 1872 ("Mémorial de l'officier du Genie"); "Manuel de pyrotechnic à l'usage de l'Artillerie de Marine," tom. ii.; "Traité de la poudre," etc., revu par Desortiaux, p. 798. 1878.

[2] Stockholm, Hamburg, Aspinwall, San Francisco, Quenast in Belgium.

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associated with silica, alumina, magnesium carbonate, calcined alum, brick-dust, tripoli, sand, boghead ashes, etc., all these being substances intervening only to a slight extent, or not at all, by their chemical composition, but only by their physical constitution and their relative proportion. They check the propagation of the molecular shocks, the harmonious succession of which gives rise to the explosive wave (p. 78). After deflagration, they are more or less modified.

3. Others, containing an active base, may themselves be separated into three groups.

4. Some dynamites (those with ammonium nitrate or potassium chlorate base) are formed by the association of nitroglycerin with an explosive substance, which explodes simultaneously without the elements of the one intervening chemically in the decomposition of the other. They might be termed *dynamites with simultaneous active base.*

5. Other *dynamites with simple combustible base* are manufactured by taking advantage of the fact that the explosion of nitroglycerin sets free a certain quantity of oxygen (3·5 per cent.) in excess of that which is necessary to convert the whole of the carbon into carbonic acid and the whole of the hydrogen into water.

There is then added to the nitroglycerin, whether pure or already mixed with an inert substance, a certain quantity of a combustible body (coal, wood sawdust, starch, straw, bran, sulphur, spermaceti, etc.) for the purpose of utilising this excess of oxygen.

6. But the quantity of oxygen is generally too small for the corresponding proportion of combustible matter, such as 1 per cent. of coal or spermaceti, or 2 per cent. of wood sawdust, or 3·5 per cent. of powdered sulphur, to be sufficient to absorb the whole of the corresponding nitroglycerin. Hence in practice the complementary substance must be employed in great excess, which constitutes the *mixed base dynamites.* We will only mention black dynamite, a mixture of charcoal and sand, capable of absorbing 45 per cent. of nitroglycerin. Such an excess of combustible matter changes the character of the chemical reaction, which may cease to be a total combustion.

7. *Dynamites with a combustible explosive base* may also be prepared by employing as combustible complement a compound explosive in itself, but which does not contain enough oxygen to undergo total combustion.

Such are gun-cotton, the several varieties of nitro-cellulose and nitro-starch, picric acid, etc.

They belong to two principal groups.

8.—(1st) Dynamites with nitrate base; such as *dynamite with black powder as base* (100 parts of black powder associated with from 10 to 50 parts of nitroglycerin).

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Dynamite with blasting powder as base.

Dynamite with saltpetre and charcoal as base.

Dynamite having as base barium nitrate and resin, or *charcoal,* with or without the addition of *sulphur.*

Dynamites having as base sodium nitrate, charcoal, and sulphur, etc.

Dynamites formed by nitroglycerin, *saltpetre* and *wood sawdust,* or *starch,* or *cellulose.*

9.—(2nd) *Dynamites having as base pyroxyl,* such as Trauzl dynamite, formed of nitroglycerin and gun-cotton in a paste.

Abel's glyoxylin, formed of the same substances, with the addition of saltpetre.

Dynamites having as base a nitrified ligneous substance (paper pulp, or wood pulp), and analogous ones.

Blasting gelatin, formed by the association of 93 to 95 parts of nitroglycerin, and 5 to 7 parts of collodion cotton.

10. We should here note that the relative proportions of nitroglycerin and of the combustible or explosive base, which are the most useful in practice, are not always those which correspond to a total combustion; either because an incomplete combustion gives rise to a greater volume of gas, or because the rapidity of decomposition and the law of expansion vary according to the relative proportions and the conditions of application.

11. It can further be seen that the inert, the simple combustible, and the explosive combustible substances may be associated in various proportions, and this constitutes fresh *dynamites with mixed base,* extremely varied.

The requirements of practice and the imagination of inventors are daily multiplying these varieties, designated by the most diversified and sometimes the most pompous names: *Hercules powder, giant powder, petralites,* etc.; but they all belong to the five foregoing types.

12. Among these practical requirements we shall point out some of those which play the most important part, independently of the question of the first cost. The most important point lies in the strength of the mixture. Indeed, the additions have generally the effect of lowering the strength, by reducing the amount of nitroglycerin. It is sought in this way to retard decomposition, so as to change the shattering agent into a propulsive agent. But if the retardation be too great, we enter into the category of the slow powders (p. 2), and lose the advantages due to the presence of nitroglycerin. There is, therefore, a practical limit to these additions, if it be desired to obtain the greatest useful effect. The use of mica, on the contrary, increases the rapidity of explosion.

The homogeneousness and stability of the mixture are of the highest importance; it is, in fact, requisite that the nitroglycerin should be entirely absorbed by the substance which serves as

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base, and that this mixture should remain uniform without chemical change and without exudations due to shocks in transport or to variations in temperature, otherwise we should be brought back to the drawbacks and dangers of pure nitroglycerin. The absorbent substance must, therefore, have a special structure opposing itself to the spontaneous separation of the nitroglycerin. Dynamites having as base ordinary sand, brick-dust, and powdered coke have thus been set aside owing to their instability.

The presence of an excess of nitroglycerin beyond the saturation point may even diminish the strength of a dynamite instead of increasing it, owing to the difference of the mode of propagation of the explosive wave in the liquid and in the porous mixture. It is in this way that the crushing effects upon a leaden block are more marked with 75 per cent. dynamite than with a richer dynamite, and even with pure nitroglycerin.

13. This tendency to separation is increased by a special property of nitroglycerin, which plays an important part in the application of all dynamites formed by this agent, viz. the solidification of nitroglycerin at about 12°. In fact, in becoming solidified, the explosive more or less completely separates itself from its absorbent, and thenceforth constitutes a new system, endowed with special properties.

On the one hand, solid nitroglycerin seems less sensitive to shocks, and especially to their transmission step by step. It requires more powerful fuses to explode it, which generally renders it necessary to reheat the cartridges in order to liquefy it, and to reconstitute the original dynamite, an operation which has occasioned numberless accidents in mines.

On the other hand, nitroglycerin thus liquefied, after having been partly separated from its absorbent by crystallisation, may not mix with it again in so intimate a manner as before, especially if the absorbent be not of good quality, and if it be submitted to pressure.

14. The degree of sensitiveness to shock of dynamites is a circumstance of fundamental importance, particularly for military applications. Thus it is necessary to put into the hands of soldiers a substance which does not explode during transport, nor under the shock of a ball. Ordinary dynamite with silica base does not satisfy this condition, which has often caused compressed gun-cotton to be preferred, though the latter is not entirely free from danger in this respect.

15. It has been attempted to gain the end in view by adding certain foreign substances to dynamites—camphor, for instance, to the amount of a few hundredth parts; but this mixture is only moderately efficacious.

The condition sought after is especially realised by blasting gelatin, formed of nitroglycerin and collodion cotton. But here

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we meet another stumbling-block; the substance requires special capsules and too great a quantity of fulminate to explode it. This must be compensated for by employing a small intermediate cartridge of compressed gun-cotton, primed itself with fulminate, which complicates the question. It appears that even in this way it is sometimes difficult to effect the explosion of blasting gelatin.

16. This technical discussion will not be further entered upon here except to observe that the absence of explosion by simple ignition, and the necessity for special detonators, are among the number of essential characteristics which distinguish dynamite from service powder and all analogous kinds.

Hence arise fresh complications in the use of these substances. Thus, owing to this circumstance and the risk of explosions by influence, the detonators should be carefully kept apart from the stores of dynamite, in magazines, and during transport. Many accidents are due to the neglect of this precaution.

17. These general notions being set forth it would require a whole volume to enter into the study and the discussion of the properties of all the dynamites proposed, or even only of those actually employed. This is why we shall confine ourselves to treating with more detail three interesting varieties of dynamite in order to show how our theories are applied to their study. They are—

1st. *Dynamite proper* with silica as base.

2nd. Dynamite with ammonium nitrate as base.

3rd. Blasting gelatin with collodion cotton as base.

§ 2. Dynamite Proper.

1. We have said above how Nobel had invented this substance to obviate the terrible effects which result from the propagation of shocks in liquid nitroglycerin. Now, dynamite proper, being less sensitive to shocks than nitroglycerin, can be transported and handled almost without danger, provided certain rules be observed.

2. For many years dynamite has been employed in mines and in tunnel boring to rupture and reduce very hard or fissured rocks, as well as in harbour and other works. It has been applied to break up blocks of stone, masses of cast or wrought iron, blocks of pyrites, beds of flint, accumulated ice, to break up and lighten soils intended for vine growing, etc., and its applications are daily being developed.

Dynamite also plays a most important part in warfare (torpedoes, mines, the destruction of palisades, the levelling of trees, buildings and bridges, the destruction of rails and railways, the bursting of cannons, etc.).

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3. Dynamite proper results, as we have said, from the association of nitroglycerin with amorphous silica. At the outset Nobel employed for this purpose *Kieselguhr*, that is, the silicious earth of Oberlohe (Hanover); but there have since been found in various places natural silicas, such as randanite (Auvergne), which answer the same purpose.

The special structure and the organic origin of these varieties of silica, formed for the greater part of shells and infusoria (Diatoms), were at first regarded as indispensable for the fabrication of dynamite. But amorphous silica, prepared by a chemical process—for instance, that resulting from the action of water on silicon fluoride—is no less suited for this preparation; it even stores up at least as large quantities of nitroglycerin (more than nine times its weight) as natural silica.

4. Dynamites are also distinguished according to their origin—as Nobel and Iboz dynamites, Vonges dynamites, etc.; and according to their strength—No. 1 dynamite, with 75 per cent. of nitroglycerin; No. 2 dynamite, with 50 per cent.; No. 3 dynamite, with 30 per cent.

5. *Preparation.* The silica is first dried in ovens, without however heating it to too high a temperature, and sifted to eliminate the large grains; then the nitroglycerin is incorporated with it. A few hundredth parts of lime or magnesia carbonates or of sodium bicarbonate are added in order to prevent the mixture from becoming acid, a transformation which is the prelude to its spontaneous decomposition.

6. *Properties.* The substance thus obtained is grey, brown, or reddish (according to the foreign ingredients), rather greasy to the touch, forming a pasty mass. It should not give rise to considerable exudations of nitroglycerin. The absolute density of dynamite is a little more than 1·60. The relative density, obtained by the gravimetric method, is 1·50 for dynamite at 75 per cent.

In preparing dynamite an apparent contraction of the materials is observed; that is to say, that the nitroglycerin occupies a volume less than the air interposed in the silica. Nitroglycerin freezing at 12°, dynamite is transformed at about this temperature, or slightly below, into a hard mass, expanding at the same time. The properties of dynamite are then extremely modified, and it requires much stronger detonators to explode it; say 1·5 grm. of fulminate, instead of 0·5. However, the explosive force remains the same. This circumstance forms one of the most serious drawbacks to the keeping and use of dynamite. Indeed the necessity for thawing it frequently occasions serious accidents, especially if this operation be effected at an open fire and without precautions. It was in this way that at Parma, in 1878, a lieutenant of cavalry having placed on a brazier a can containing one kgm. of dynamite, an

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explosion immediately occurred, eighty persons being killed or wounded.

Moreover, thawing may occasion exudations of pure nitroglycerin, the latter expanding by the fact of solidification. It is thus exposed and may explode by subsequent shock of friction. It is sometimes enough to bring about an accident, to cut a frozen cartridge with an iron tool. Ramming is even dangerous with it. Moreover, frozen dynamite has not lost the property of exploding by influence.

7. *Action of heat.* Dynamite, submitted to the action of a gentle heat, undergoes no change, even under the prolonged influence (an hour) of a temperature of 100°. Heated rapidly, it takes fire near 220°, like nitroglycerin. If ignited, it burns slowly and without exploding; but if it be enclosed in a hermetically sealed vessel with resisting walls, it explodes under the influence of heating. The same accident is sometimes produced in the inflammation of a large mass of dynamite, owing to the progressive heating of the interior parts, which brings the whole mass to the temperature of explosive decomposition.

Dynamite, moreover, becomes more sensitive to shock, as do also explosive substances in general, according as it is raised nearer to temperature of decomposition.

Direct solar light can cause a slow decomposition, as with all the nitro and nitric compounds. Electric sparks, generally speaking, ignite dynamite without exploding it, at least when operating in the open air.

8. *Spontaneous decomposition.* Dynamite prepared with neutral nitroglycerin appears to keep indefinitely if care be taken to add to it a small quantity of calcium carbonate, or alkaline bicarbonate, thoroughly mixed. Contact with iron and moisture changes it in course of time. Dynamite which has commenced to undergo change becomes acid and sometimes explodes spontaneously, especially if contained in resisting envelopes. Nevertheless, neutral and well-prepared dynamite has been kept for ten years in a magazine without loss of its explosive force.

9. *Action of water.* Water brought into contact with dynamite gradually displaces the nitroglycerin from the silica. This action is slow but inevitable. It tends to render all wet dynamite dangerous. However, ordinary dynamite hardly attracts the atmospheric moisture.

It has been observed that a dynamite made with wood sawdust can be moistened, then dried without marked alteration, provided the action of the water has not been too prolonged. Fifteen to twenty per cent. of water may be added to cellulose dynamite, rendering it insensible to the shock of a ball without depriving it of the property of exploding by a strong fuse. But nitroglycerin is then separated under a slight pressure.

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10. *Action of shock.* Dynamite requires a much more violent shock than nitroglycerin to explode it. It explodes by the shock of iron on iron, or of iron on stone, but not by the shock of wood on wood.

Dynamite is the more sensitive the more nitroglycerin it contains.

When dynamite is struck with a hammer, the part directly affected by the shock alone explodes, the surrounding portions being simply dispersed.

Owing to this circumstance the effects may vary greatly, unless the dynamite be contained in a resisting and completely filled envelope, or placed at the bottom of a receptacle. It explodes by the direct shock of a ball at a distance of 50 m., and even more, a very important matter in military applications.

11. The detonation of dynamite in tubes entirely filled with this substance propagates itself with a speed of about 5000 mm. per second.

12. Its explosion, when complete, does not produce noxious gases, like gunpowder; but if it burn by simple inflammation (miss-fires), it produces nitric oxide, carbonic oxide, and nitrous vapour, which are deleterious (p. 283).

13. The heat liberated by the sudden decomposition of dynamite is the same as its heat of total combustion, and proportionate to the weight of nitroglycerin contained in the dynamite.

It can therefore be easily calculated from the data on page 424.

14. The volume of gases liberated by any dynamite, and the theoretical pressure which it can develop, are also calculated in this way, taking into account the volume occupied by the silica (see p. 425), and the heat absorbed in raising its temperature.

The experiments of Sarrau and Vieille on this question have been described above.

15. It will be shown in a general way that thermal theories favour the employment of dynamite. In the first place, dynamite is less shattering than nitroglycerin, because the heat liberated is shared between the products of explosion and the inert substance. In consequence there is a less rise in temperature, which diminishes the initial pressures proportionately.

For instance, the silica and anhydrous alumina, which may be mixed with nitroglycerin, have nearly the same specific heat (0·19) as the gaseous products of explosion of the latter at constant volume. Weight for weight, and in a completely filled space, they will lower the temperature, and consequently the initial pressure by half.

For an equal weight of nitroglycerin the shattering properties

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will therefore be diminished proportionately to the weight of the inert matter in the mixture; while the maximum work will retain the same value, being always proportional to the weight of nitroglycerin.

The same circumstances will render the propagation of simple ignition of a small portion of the mass into the neighbouring parts more difficult, since the latter explode only when raised suddenly to a temperature approaching 200°. Hence the explosion produced by a detonator requires a greater initial disturbance in order to take place.

If deflagration be produced by the shock of a hard body, or of a fulminating fuse, the solid particles interspersed in the liquid divide the energy of the shock between the inert and the explosive substance, in a proportion depending on the structure of the inert substance. The latter thus changes the law of explosion; it opposes itself to some extent to the propagation of the explosive wave, except in the case of extremely violent shocks, and introduces an extreme diversity into the phenomena, as follows from the experiments of Nobel, and those of Girard, Millot, and Vogt, on nitroglycerin mixed with silica, alumina, ethal, or sugar.

It is, moreover, evident that the useful effects of the inert substance could only be completely produced when the mixture is homogeneous, and without any separation of liquid and nitroglycerin, for the liquid which has exuded retains all its properties, hence the necessity of the special structure in a solid substance.

§ 3. Dynamite with Ammonium Nitrate Base.

1. This substance is very interesting on account of the great energy which is derived both from nitroglycerin and ammonium nitrate, whether associated or not with a complementary combustible substance.

It has been proposed on various occasions by inventors, with certain variations due to the introduction of the complementary bodies (charcoal, cellulose, etc.), the latter being for the double purpose of utilising the excess of oxygen supplied both by nitroglycerin and ammonium nitrate, and for completing the absorbent properties of the substance.

But this dynamite presents a certain drawback, because ammonium nitrate is hygroscopic, especially in an atmosphere saturated with moisture. Moreover, water immediately separates nitroglycerin from it.

2. The relative proportions of nitroglycerin, ammonium nitrate, and combustible substances may vary extremely, even when it is subjected to the condition of a total combustion. We shall consider only the mixtures in which charcoal constitutes the

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combustible substance, and for the sake of simplicity the charcoal will be considered as pure carbon.

All systems which satisfy the condition of total combustion reduce themselves to the following formula:—

$$x[C_3H_2(NO_3H)_3 + \tfrac{1}{2}C] + y(NO_3NH_4 + C).$$

They produce

$$(3\tfrac{1}{4}x + \tfrac{1}{2}y)CO_2 + (2\tfrac{1}{2}x + 2y)OH_2 + (1\tfrac{1}{2}x + y)N_2.$$

The corresponding weight is

$$(230x + 86y) \text{ grms.}$$

The heat liberated (gaseous water) is equal to

$$325{\cdot}7x + 79{\cdot}2y;$$

Or, for 1 kgm.,

$$\frac{1000}{230x + 86y} = (235{\cdot}7x + 79{\cdot}2y).$$

The volume of the gases is

$$(7\tfrac{1}{4}x + 4\tfrac{1}{2}y)\ 22{\cdot}32 \text{ litres } (1 + at) = \frac{0{\cdot}760}{H}.$$

The permanent and the theoretical pressure at a density of charge $\frac{1}{n}$ are immediately deduced from the above data.

3. For instance, let

$$x = 1;\ y = 16$$

be the corresponding weight: 230 + 1376 = 1606 grms.

The percentage of the immediate composition will be—

Nitroglycerin	14·1
Ammonium nitrate	79·6
Charcoal	6·3

4. The heat liberated = 1593 Cal. (gaseous water), or 1938 Cal. (liquid water); or, for 1 kgm., 992 Cal. gaseous water, or 1207 Cal. liquid water.

5. The reduced volume of the gases (gaseous water) = 1769 litres, or 642 litres (liquid water); or, for 1 kgm., 1101 litres gaseous water, or 400 litres liquid water.

6. The permanent pressure (liquid water) $= \frac{400 \text{ atm.}}{n - 0{\cdot}39}$, with the usual reservation as to the liquefaction of the carbonic acid when n falls below a certain limit.

7. The theoretical pressure $= \frac{17176 \text{ atm.}}{n}$, a value higher than the theoretical figure for ordinary 75 per cent. dynamite (p. 425).

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This is in conformity with the practical tests which point to the approximate equal power of 60 per cent. dynamite and the mixture formed of 75 parts of ammonium nitrate, 3 parts of charcoal, 4 parts of paraffin, and 18 parts of nitroglycerin.

§ 4. Dynamite with Nitrocellulose Base.

1. The association of nitroglycerin with gun-cotton was first proposed in 1868 by Trauzl, in Austria; but the product thus obtained was dangerous and difficult to manufacture, and was not adopted in practice. However, at the present day there is a tendency to return to active base dynamites of a similar formula (dualines). They are sometimes associated with potassium nitrate (lithofracteur), etc. Mixtures containing 40 parts of nitroglycerin and 60 parts of gun-cotton or nitro-lignite, with the addition of 2 per cent. of ammonium carbonate, are those which are more especially manufactured. These mixtures do not correspond to a perfect combustion, but they will produce effects very closely approaching the mean of their components. Dynamite with ligneous nitrocellulose base is somewhat less sensitive to shock and freezing than that containing gun-cotton. If potassium nitrate be superadded it allows of the combustion being completed, but it increases the sensitiveness.

2. Some years since Nobel conceived the idea of forming a compound of quite a different order by dissolving collodion cotton in nitro-glycerin in the proportion of 93 parts of the latter and 7 parts of the former, and in this way obtained the substance called blasting gelatin, explosive gelatin, or gum dynamite, a clear, yellow, gelatinous, elastic, transparent compound, more stable than ordinary dynamite, especially from a physical point of view, for it gives rise to no exudation, even by pressure. It is unchangeable by water (see further on). Lastly, it is much more powerful than Kieselguhr dynamite and comparable in this respect to pure nitroglycerin.

By adding to blasting gelatin a small quantity of benzene, or, better still, of camphor (from 1 to 4 per cent.), it is rendered insensible to mechanical actions which cause the explosion of ordinary dynamite, such as friction, the shock of a bullet at a short range, etc. Its strength is appreciably diminished by this mixture, but it is no longer developed except under the influence of very strong charges of fulminate or of a special primer formed of nitrohydrocellulose (4 parts), nitrocellulose and nitroglycerin (6 parts), which itself may be ignited by a small charge of fulminate.

The work of the initial shock necessary to explode blasting gelatin has been calculated at six times that which would be required for ordinary dynamite, *cæteris paribus*, a difference

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which is doubtless attributable to the cohesion of matter; that is to say, to the greater mass of particles in which the energy of the shock transformed into heat causes the first explosion which is the origin of the explosive wave (p. 54).

Owing to these circumstances blasting gelatin is far less sensitive to explosions by influence. All these conditions are very favourable to its use as an explosive for military purposes.

3. The properties of this substance will now be more particularly considered. Blasting gelatin does not absorb water; it merely turns white on the surface under this influence, owing to the solution of the nitroglycerin contained in the superficial stratum, but the action does not go any further. The collodion cotton, separated by the action of the water on the first stratum of substance, being insoluble in this agent, envelops the whole of the rest of the mass in a protecting film. Blasting gelatin therefore remains unaltered, even after having been kept for forty-eight hours under running water. The explosive force has been found to be the same after this test.

Neither does freezing change its shattering force, but it causes it partly to lose its insensibility to shock.

4. The density of blasting gelatin is 1·6, *i.e.* equal to that of nitroglycerin, as might have been expected from its composition and its homogeneous structure without pores. This density is higher than the apparent density of dry gun-cotton (1·0) or damp gun-cotton (1·16), which constitutes a real and important advantage.

5. Blasting gelatin burns in the open air without exploding, at least when small quantities are operated upon and a previous heating is avoided. It has been kept for eight days at 70° without being decomposed.

After having been kept for two months between 40° and 45° it lost the half of the camphor and a small quantity of nitroglycerin without further alteration.

Slowly heated it explodes towards 204°.

If it contains 10 per cent. of camphor, it no longer explodes, but it fuses.

6. Let us now estimate the strength of blasting gelatin by our ordinary calculations.

As an example, a blasting gelatin formed of 91·6 parts of nitroglycerin and 8·4 parts of collodion cotton, which are the proportions corresponding to a total combustion.

The collodion cotton is here taken as corresponding to the formula—

$$C_{24}H_{22}(NO_3H)_9O_{11}.$$

Such a dynamite is formed in the proportions—

$$51C_3H_2(NO_3H)_3 + C_{24}H_{22}(NO_3H)_9O_{11}.$$

Its equivalent weight is 12,360 grms.

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The explosion produces

$$177CO_2 + 143H_2O + 81N_2.$$

7. The heat liberated by its explosion is equal to 19381 Cal. (gaseous water) or 2241 Cal. (liquid water); or, for 1 kgm., 1535 Cal. (gaseous water), or 1761 Cal. (liquid water).

8. Reduced volume of the gases = 8950 litres (gaseous water) or 5759 litres (liquid water); or, for 1 kgm., 709 litres (gaseous water), or 456 litres (liquid water).

9. The permanent pressure (liquid water) $= \frac{456 \text{ atm.}}{n - 0{\cdot}41}$, with the usual reservations.

10. The theoretical pressure $= \frac{19220 \text{ atm.}}{n}$, value nearly identical with that of nitroglycerin (p. 425).

It might have been supposed that the pressure and the heat developed would have been greater owing to the complete utilisation of the oxygen, but there is a compensation on account of the greater loss of energy which takes place at the outset in the union of the elements, and afterwards in the combination of nitric acid with the cellulose, which liberates 11·4 Cal. per equivalent of fixed acid instead of 4·9 Cal. liberated in the case of nitroglycerin (see p. 282).

Hence it will be seen that blasting gelatin considerably surpasses ordinary dynamite in the ratio of 19 : 14 according to theory. The ratio of the actual effects of the two substances has been estimated by Hess, by the aid of practical tests based on the rupture of strong pieces of wood. It has been found to approach the numbers 78 : 56, which notably are in accord.

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CHAPTER VII.

GUN-COTTON AND NITROCELLULOSES.

§ 1. Historical.

1. In 1846 Schönbein proposed to replace service powder by a new substance, the composition of which he kept a secret. This was gun-cotton, the discovery of which is the starting-point of the works since accomplished with the new explosive substances. In 1832 Braconnot and Pelouze had already made known some similar nitric compounds.

Numerous experiments carried out up till 1854 led to gun-cotton being regarded as more powerful for equal weights than black gunpowder, that it possessed shattering properties which hardly admitted of its continued use in firearms. Soon, terrible explosions and accidents in powder factories[1] gave evidence of the existence of spontaneous decompositions, which put a stop to its manufacture almost everywhere; nevertheless, experiments were still carried out in Austria, under the direction of Lenck, until the occurrence of a fresh explosion in a magazine at Simmering in 1862. Another explosion occurred in 1865 at Wiener-Neustadt.

2. In England, however, Abel succeeded in almost entirely removing risks by a very careful process of manufacture, namely, by reducing the cotton to pulp, which enabled it to be more completely washed, and finally, by the compression of the cotton (1865) by hydraulic presses.

Compressed gun-cotton thus came into use. Brown discovered in 1868 that it could be detonated by means of mercury fulminate.

The explosion which happened in 1871 in the Stowmarket factory, and in which twenty-four persons perished, was attributed, rightly or wrongly, to imperfect supervision, and the manufacture of compressed gun-cotton is still carried out in England. It has been carried out also in France for some time at the "Moulin Blanc" factory.

[1] Bouchet and Vincennes, 1847.

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3. Gun-cotton is practically only used for military purposes, since its high price prevents it becoming a rival of dynamite, which, besides, is more easily adapted to the requirements of miners.

In Austria, Russia, and France, even up till recently, dynamite has been preferred to it as a war explosive, whereas in England and Germany gun-cotton has the preference. The Marine Artillery in France[1] also uses it, and the French army authorities evince a tendency to go back to its use on account of its safer preservation.

4. However, gun-cotton being, like dynamite, susceptible of detonation from the shock of a ball at a short distance, endeavours have been made to reduce this sensitiveness. In order to effect this it suffices to incorporate with it from ten to fifteen per cent. of water or paraffin. Damp gun-cotton is much better able to resist mechanical agents.

In this state it cannot be inflamed by contact with a body in ignition, or by spontaneous decomposition. Gun-cotton, when mixed with paraffin, is also less sensible to shock, but it is not safe from the risk of inflammation.

On the other hand, the detonation of moistened or paraffined gun-cotton is more difficult; it requires the employment of a very strong dose of fulminate, or a small hand-made cartridge of dry gun-cotton primed with fulminate.

The presence of water, as also of paraffin, further lessens the force of the explosion.

The application of water is subject to variations owing to spontaneous evaporation, which is a serious difficulty.

In the German army paraffin is employed. The application of this is simpler, and it is not subject to variations on account of the weather. Nevertheless, sensibility to detonators does not appear to be the same in paraffined gun-cotton which has been recently or for some time prepared, probably on account of the change in structure, which is the result of the slow crystallisation of the paraffin.

5. Gun-cotton does not, like nitroglycerin, contain a sufficient quantity of oxygen for the combustion of its elements; hence the proposal to associate it with potassium, barium, or ammonium nitrate, or with potassium chlorate; bodies which would supply it with oxygen.

Abel's glyoxyline contains potassium nitrate and nitroglycerin.

The most varied compounds have from this point of view been proposed, and continue to be proposed daily. We shall particularly mention Schultze powders, formed by nitrified

[1] See "Mémorial des Poudres et Salpêtres" (Rapport sur l'emploi du coton-poudre aux opérations de guerre), par H. Sebert, Commissions des Explosive Substances, p. 109. 1882.

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wood-pulp associated with various nitrates, an explosive which has assumed some importance recently.

6. In the following paragraphs we shall merely treat of ordinary gun-cotton alone and when with water or nitrates, these three substances being regarded as types. We shall, as usual, regard them chiefly with reference to the degree of heat liberated, the volume of gases, and the pressures developed.

§ 2. Nitro-celluloses: their Composition.

1. The nitrification of cellulose under its various forms (cotton, paper, straw, wood-pulp, etc.) is accomplished by means of nitric acid of various degrees of concentration, with or without the addition of sulphuric acid, and working at different temperatures. The products are numerous, and they have been the object of many researches. Here we shall content ourselves by reproducing the results of the most recent experiments, namely, those by Vieille [1] carried out at 11°, in the presence of an excess of acid sufficient to prevent the water formed by the reaction modifying the composition to any appreciable extent.

The highest nitrification is obtained with nitro-sulphuric mixtures; it corresponds sensibly to the formula of an endecanitric cellulose—

$$C_{24}H_{15}(NO_3H)_{11}O_9.$$

This is gun-cotton intended for military purposes.

With nitric acid alone, corresponding to the composition

$$(NO_3H + \tfrac{1}{4}H_2O),$$

and when experimenting at 11°, we obtain a decanitric cellulose; that is to say, less rich in acid—

$$C_{24}H_{20}(NO_3H)_{10}O_{10},$$

a body which is completely soluble in acetic ether, but almost insoluble in a mixture of alcohol and ether. This is still gun-cotton.

When the acid is rather more diluted—

$$(HNO_3 + 34H_2O),$$

it yields collodion cotton, the composition of which is very similar to that of the enneanitric and octonitric celluloses—

$$C_{24}H_{22}(NO_3H)_9O_{11}, \text{ and } O_{24}H_{24}(NO_3H)_8O_{12},$$

bodies which are soluble in acetic ether and in a mixture of alcohol and ether.

With the acid $NO_3H + \frac{1}{2}H_2O$, a cellulose is obtained which answers to the characteristics of a heptanitric compound—

$$C_{24}H_{26}(NO_3H)_7O_{13},$$

[1] "Comptes rendus des séances de l'Académie des Sciences," tom. xcv. p. 132. 1882.

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yet still preserving the aspect of the cotton, but which becomes gelatinous without actually dissolving in a mixture of alcohol and ether and in acetic ether.

If the acid is more diluted, such as

$$(NO_3H + \cdot 75H_2O),$$

the cotton becomes dissolved in such an acid, producing a viscous liquor which can be precipitated by water. The product obtained is similar in its characteristic features to hexanitric cellulose—

$$C_{24}H_{28}(NO_3H)_6O_{14}.$$

It swells in acetic ether without dissolving. A mixture of alcohol and ether does not act on the substance.

With the acid NO_3H mixed with + 1·375 to 1·5 H_2O, we obtain friable products, without any action on acetic ether or on the mixture of alcohol and ether, and which vary between the following formulæ:—

$$C_{24}H_{30}(NO_3H)_5O_{15}$$
$$C_{24}H_{32}(NO_3H)_4O_{17}.$$[1]

With a more diluted acid, the nitrification is incomplete, the products still being darkened by iodine; that is to say, it is no longer possible to distinguish the nitro compounds properly so called from their mixture with the unaltered cellulose.

§ 3. Gun-cotton properly so called.

1. Gun-cotton[2] preserves the appearance of cotton, although it is slightly rougher to the touch. It is not hygroscopic, and it also possesses the property of becoming electrified by friction. Plates for electric machines have even been constructed with nitrified paper.

Gun-cotton is soluble in acetic ether, but insoluble in most other solvents (water, alcohol, ether, acetic acid, and ammoniacal copper oxide).

It may be moistened, and when dried resumes its properties.

When in lumps, its apparent density is only 0·1; if it be

[1] Table of the volumes of nitric oxide obtained by Schlœssing's process from various celluloses by Vieille. One grm. gives—

Endecanitric cellulose	Gun-cotton	214	c.c.
Decanitric „		203	„
Enneanitric „	Collodion cotton	190	„
Octonitric „		178	„
Heptanitric „	... ...	162	„
Hexanitric „	... ...	146	„
Pentanitric „	... ...	128	„
Tetranitric „	... ...	108	„

[2] For its preparation see "Traité sur la poudre," par Upman et Meyer, traduit et augmenté par Desortiaux, etc., p. 350.

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twisted into thread, it increases to 0·25; when subjected, in the form of pulp, to hydraulic pressure, it becomes 1·0; but these densities are apparent, the absolute density of gun-cotton being 1·5.

Nitrohydrocellulose prepared with cellulose disintegrated by hydrochloric or sulphuric acid (A. Girard's process) has a pulverulent form, which is very convenient for practical use. Its composition and the force are the same as for gun-cotton.

2. Gun-cotton is an extremely explosive compound, which is ignited by contact with a heated body or by shock, or, again, when it is raised to a temperature of 172°. It burns suddenly, with a large yellowish-red flame, but almost without smoke or residue, and liberates a large volume of gas (carbonic acid, carbonic oxide, nitrogen, steam, etc.).

Compressed gun-cotton previously heated to 100° may explode when ignited. It is, therefore, more liable than dynamite to explode on simple inflammation.

Gun-cotton kept at 80° to 100° decomposes slowly, and may end by inflaming.

It has been shown that a thin disc of compressed gun-cotton may be pierced by a ball without explosion; but if the thickness of the disc be increased, or if resisting envelopes be used, an explosion occurs.

3. Sunlight causes it to undergo slow decomposition.

4. Gun-cotton should be neutral to litmus, when it has been carefully freed from all acid products by washing with alkali. Nor should it emit acid fumes even, after keeping for some time. A little sodium or ammonium carbonate is incorporated with it to increase its stability.

In the French navy, gun-cotton is submitted to a heat test, which consists in heating it to 65°, until it gives off sufficient nitrous vapour to turn the iodised starch paper blue, or more simply to redden litmus. It should stand this test for eleven minutes. The heat test may be carried out either on the raw material or on the washed product (the washing frees it from alkaline carbonates), compressed between blotting paper, dried at a low temperature, then left some time in the open air.

5. The indefinite stability of gun-cotton has always been regarded as doubtful, both by reason of its chemical constitution and by the presence of the accessory products arising from the original reaction or formed by accidental causes, which it is hardly possible to avoid indefinitely. A slow decomposition produced in this way sometimes becomes considerably accelerated by the heat which it liberates and by the reaction of the products originally formed on the rest. It may become violent, and end by exploding (see p. 45).

Nevertheless, gun-cotton has been preserved for ten years and more without any alteration. It has also been kept dry on

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board vessels during long voyages, even in high temperatures in the tropics.

6. Gun-cotton is very susceptible to explosions by influence. According to experiments made in England, a torpedo, even placed at a long distance, may explode a line of torpedoes charged with gun-cotton.

7. The velocity of the propagation of the explosion in metallic tubes filled with pulverised gun-cotton has been found to be from 5000 to 6000 mms. per second in tin tubes, and 4000 in leaden tubes (Sebert).

Gun-cotton loosely exposed in the open air burns eight times as quickly as powder (Piobert).

8. It is admitted that the effect of gun-cotton in mines is very nearly the same as that of dynamite for equal weights. It requires stronger detonation, and it gives rise to a large quantity of carbonic oxide, which is sometimes difficult to disperse, because the earth remains impregnated with the gas. Carbonic oxide being very deleterious, the use of gun-cotton is dangerous to workmen in mines. But the form of compressed gun-cotton is more convenient, because it does not require resisting envelopes, and because it preserves the form which is given to it. Besides, it is less sensitive to shock by reason of its special structure. Its use for firearms has been abandoned.

9. Let us now examine gun-cotton a little closer from a theoretical point of view. Its force depends upon its composition, and upon the nature of the products, which vary with the density of the charge; that is to say, with the pressure developed.

10. We have, at p. 288, given a summary of the very interesting researches of Sarrau and Vieille on this question.

Let us simply remember that the substance studied by these authors contained—

C	24·4
H	2·4
N	12·8
O	56·5
Water	1·4
Ash	2·5

that is to say, abstracting the water and the ash—

C	25·4
H	2·5
N	13·3
O	58·8

the formula $C_{24}H_{18}(NO_3H)_{11}O_9$ requires—

C	25·2
H	2·6
N	13·5
O	58·7

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11. The equivalent of this substance is 1143.

12. The heat liberated by the formation of gun-cotton from the elements under constant pressure—

$$C_{24} \text{ (diamond)} + H_{29} + N_{11}O_{42},$$

amounts to 624 Cal. for 1143 grms., or 546 Cal. for 1 kgm.

The heat of formation of collodion cotton—

$$C_{24} + H_{31} + N_9 + O_{38} = C_{24}H_{22}(NO_3H_9)O_{11},$$

is 696 Cal. for 1053 grms., or 661 Cal. for 1 kgm.

Soluble gun-cotton made in Norway is very near this composition.

13. The heat liberated in the total combustion of gun-cotton by free oxygen—

$$2[C_{24}H_{18}(N_2O_3H)_{11}O_9] + O_{41} = 48CO_2 + 29H_2O + 11N_2,$$

at constant pressure, is 2633 Cal. for 1143 grms. (water liquid), or 2488 Cal. (water gaseous). Say for 1 kgm. of gun-cotton, 2302 Cal. (water liquid), or 2177 Cal. (water gaseous).

The total heat of combustion of collodion cotton—

$$2[C_{24}H_{22}(NO_3H)_9O_{11}]O_{51} = 48CO_2 + 31H_2O_2 + 9N_2,$$

at constant pressure, the water being liquid, + 2627·5 Cal.; the water being gaseous, + 2474·5 Cal.

It will be seen that it is nearly the same at equal equivalents as for gun-cotton.

For 1 kgm. of collodion we should have 2428 Cal. (water liquid), 2351 Cal. (water gaseous).

14. The heat of decomposition of gun-cotton in a closed vessel, found by experiment at a low density of charge (0·023), amounts to 1071 Cal. for 1 kgm. of the substances, dry and free from ash, or 1225 Cal. for 1143 grms. (water liquid).

We proceed to compare this result with the heat calculated from the equation for the decomposition.

15. *Equation for the decomposition.* From the analysis of the products, the decomposition of the gun-cotton which yielded this quantity of heat practically agreed with the following equation (low densities of charge):—

$$(1)\ 2[C_{24}H_{18}(NO_3H)_{11}O_9] = 30CO = 18CO_2 + 11H_2 + 18H_2O + 11N_2.$$

But the quantity of heat changes with the equation of decomposition, the latter approximating to

$$(2)\ 24CO + 24CO_2 + 12H_2O + 17H_2 + 11N_2$$

for high densities of charge, according to Sarrau and Vieille (p. 289). There is, moreover, no nitric oxide under these conditions.[1]

[1] Karolyi, Sarrau and Vieille.

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On the contrary, in a miss-fire (progressive combustion) the carbonic oxide increases and nitric oxide appears (p. 289).

We shall treat here only of the explosive combustion.

16. Let us now calculate the heat liberated at constant pressure.[1] According to equation (1), which corresponds to low densities of charge, the reaction liberates 1230 Cal. (water liquid), or 1140 Cal. (water gaseous).

That is to say, for 1 kgm.,[2] 1076 Cal. (water liquid), or 997·7 Cal. (water gaseous).

According to equation (2), which represents the limit of reaction for high densities of charge, we should have 1228 Cal. (water liquid), or 1168 Cal. (water gaseous). That is to say, for 1 kgm., 1074 Cal. (water liquid), or 1022 Cal. (water gaseous).

It will be remarked that the heat liberated is practically the same according to equations (1) and (2). It therefore varies but little with the density of charge, an observation which appears applicable to explosive substances in general. Thus the numbers 1074 Cal., and 1076 Cal., which correspond to the two equations, are very close to each other, and also to the figure 1071 Cal. found by experiment.

17. The volume of the reduced gases, calculated from equation (1), will be 781 litres (water liquid), or 982 litres (water gaseous); that is to say, for 1 kgm.,[2] 684 litres, or 849 litres. Sarrau and Vieille found 671 litres, with a substance leaving 2·4 per cent. of ash, which agrees. According to equation (2), the volume of the gases will be the same, the water being supposed liquid; it would be raised to 743 litres per kilogramme, the water being gaseous. Hence the volume of the gases does not change much with the density of charge.

18. The permanent pressure according to equation (1) (low densities) $= \frac{684 \text{ atm.}}{n - 0{\cdot}14}$. This formula is only applicable for densities $\frac{1}{n}$ low enough for the carbonic acid not to be liquefied.

19. The theoretical pressure, from equation (1), $= \frac{16400 \text{ atm.}}{n}$.

From equation (2) $= \frac{16750 \text{ atm.}}{n}$

Sarrau and Vieille actually found, by means of the crusher and for densities of charge $\frac{1}{n}$, the following pressures, P′ expressed in kilogrammes :—

[1] At constant volume these figures must be increased by one per cent.

[2] The substance supposed dry and free from ash.

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$\frac{1}{n}$		P.		P'.
0·10	...	1185	...	11850
0·15	...	2205	...	14700
0·20	...	3120	...	15600
0·30	...	5575	...	18600
0·35	...	7730	...	22100
0·45	...	9760	...	21700
0·55	...	11480	...	21500

But these results should be interpreted in accordance with their new researches on the calibration of "crushers" (p. 23). The latter gave for $\frac{1}{n} = 0{\cdot}20$, a maximum pressure of 1985 kgm.; which would make $\frac{P'}{n} = 9825$ kgm. The limit $\frac{P'}{n}$, that is, the specific pressure, relating to gun-cotton would therefore seem to need to be reduced to about 10,000 kgm., in round numbers, for high densities of charge. The theoretical pressure calculated from our formula would, on the contrary, be applicable to low densities. To obtain the maximum effect of gun-cotton, theory, in accordance with the latest experiments, shows that this powder must be compressed and reduced to the smallest possible volume. For the initial pressures are thereby increased.

20. Let us now compare gun-cotton with other explosive substances. It is especially distinguished by the magnitude of the initial pressures. Thus, according to theory, the initial pressure will be more than treble that of ordinary powder, which is, in fact, the empirical ratio given by Piobert.[1] This theoretical pressure, calculated from the reactions of the final state, will, moreover, be diminished in practice, as in the case of ordinary powder, owing to the incomplete state of combination of the elements and the complexity of the compounds which tend to be formed. Hence results a less sudden and more regular expansion, following upon a combination which has become more complete during cooling.

On the contrary, pure nitroglycerin, weight for weight, realises a work greater by half than gun-cotton, the initial pressure being nearly the same. It is not surprising, therefore, that nitroglycerin should have been found preferable for industrial purposes, at least in the form of dynamite; the more so as the latter needs no previous compression, is easier to divide, and, above all, more economical. But it is easier to distribute non-compressed gun-cotton in a uniform manner over a considerable space, which offers certain advantages in practice.

[1] "Traité de l'Artillerie," 2e édition, p. 496.

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§ 4. Wet Gun-cotton.

1. We have explained how it has been found advisable to employ gun-cotton saturated with water, in order to lessen its sensitiveness to shock and to render its direct inflammation impossible, which limits the risks due to a fire. Three per cent. of water is sufficient to diminish the sensitiveness, but more than 11 per cent. is required to prevent direct inflammation. The standard quantity is 15 per cent. of water; but it is difficult to maintain constant and uniform in the whole mass. Thus regular saturation, followed by compression, leaves about 25 per cent. of water in the mass, which renders a partial drying necessary. Besides, the moist substance, if it be not kept in hermetic receptacles, tends to lose the water by spontaneous evaporation.

2. Damp gun-cotton retains the property of exploding under the influence of a powerful fulminate detonator, or of a small intermediate cartridge of gun-cotton dry, or mixed with nitrate, with fulminate cap. Thus a torpedo containing 100 kgm. of gun-cotton requires a priming cylinder containing 0·560 kgm. of dry gun-cotton. It will be useful to examine the influence of the water thus introduced on the pressures developed.

3. Granted that the chemical reaction is the same as with high densities of charge (which, however, has not been verified), the heat liberated remains the same. The volume of the gases produced by gun-cotton also remains the same, whether it be calculated from that of the permanent gases alone, or the water derived from the gun-cotton be supposed to retain the gaseous state at the first instant of the explosion; an hypothesis which the experiments made on the explosive wave (p. 99) justify us in regarding as possible. Condensation will, moreover, take place almost immediately; the water vapour thus ceasing to be active beyond the first instant.

Nevertheless, the water imprisoned in gun-cotton also absorbs heat, and may even be regarded as assuming, either wholly or partly, the gaseous state, simultaneously with the water produced by the reaction.

We will calculate the pressure developed at the moment of explosion according to the various hypotheses.

4. Take, for example, gun-cotton with the addition of 20 per cent. of water—

$$C_{24}H_{18}(NO_3H)_{11}O_9 + 26H_2O,$$

and gun-cotton with 10 per cent. of water—

$$C_{24}H_{18}(NO_3H)_{11}O_9 + 13H_2O.$$

The heat liberated by decomposition with a high density of charge will be 1168 Cal. (water gaseous), or 1022 Cal., for 1 kgm. of the dry substance. This heat falls to 908 Cal. for the

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same weight of dry gun-cotton with 20 per cent. of added water. It is 1038 Cal. with only 10 per cent. of added water. This makes, in other terms, for 1 kgm. of the damp substance containing 16·7 per cent. of water, 662 Cal., and for 1 kgm. of the substance containing 9·1 per cent. of water, 882 Cal., the whole of the water being supposed gaseous. The heat is therefore reduced by a fifth in the latter case, and by a third in the former, owing to the vaporisation of the added water.

5. The volume of the reduced gases will be for 1 kgm. of the dry substance, with 20 per cent. of added water, 1563 litres; or 1139 litres for 1 kgm. damp.

We shall have further, for 1 kgm. of dry matter with 10 per cent. of added water, 1272 litres; or 1133 litres for 1 kgm. of the damp substance.

The gaseous volume is therefore increased by the addition of water, as might be expected, supposing vaporisation to take place.

6. The permanent pressure $= \frac{391 \text{ kgm.}}{n - 0{\cdot}31}$ for the substance with 20 per cent., and $\frac{426 \text{ kgm.}}{n - 0{\cdot}23}$ with 10 per cent. of water added, with the usual reservations regarding the limits of liquefaction of carbonic acid.

7. The *theoretical pressure* $= \frac{9112 \text{ kgm.}}{n}$ for the substance with 20 per cent., and $\frac{12560 \text{ kgm.}}{n}$ with 10 per cent. of added water. It will be seen that it is diminished by a third in the latter case, and that it is reduced almost to the half in the case of the most hydrated substance.

8. *Paraffined gun-cotton.* Instead of adding water to gun-cotton it has also been proposed to paraffin it, which yields mixtures which are more stable and even capable of being cut and wrought by tools working at high speeds. But it is difficult to render them uniform, unless by adding so great a quantity of paraffin that the mixture only explodes with great difficulty; 100 parts of gun-cotton absorb as much as 33 of paraffin.

Hence the operation is often confined to paraffining the cartridges superficially. To explode paraffined gun-cotton an auxiliary cartridge of ordinary gun-cotton is employed, ignited by a fulminate detonator.

9. The use of camphor and plastic substances diminishes still further the liability of gun-cotton to explode. We may also mention here *celluloid*, a variety of nitro-cellulose, nearly corresponding to $C_{24}H_{24}(NO_3H)_8O_{12}$, to which camphor and

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various inert substances are added so as to render it non-sensitive to shock. This product may be worked with tools, in the manner of ivory, and is very plastic when heated towards 150°. But it must not be forgotten that it then tends to become sensitive to shock, and that large quantities of such substances might become explosive during a fire, owing to the general heating of the mass and the evaporation of the camphor. Heated celluloid may even explode, when greatly compressed, and press accidents have occurred in factories. When maintained at 135° in an oven celluloid decomposes quickly. This is not all, for in an experiment made in a closed vessel at 135°, and the density of charge 0·4, it ended by exploding, developing a pressure of 3000 kgm.

It is therefore a substance the working of which calls for certain precautions, though it is not explosive under ordinary circumstances, even with very powerful detonators.

§ 5. "Nitrated" Gun-cotton.

Mixture formed with ammonium nitrate.

1. We will examine gun-cotton mixed with ammonium nitrate, and also with potassium nitrate, these two products having been studied in a special manner by Sarrau and Vieille.

We will first observe that gun-cotton—

$$C_{24}H_{18}(NO_3H)_{11}O_9 = 1143 \text{ grms.},$$

requires 41 equivalents of oxygen (328 grms.) for complete combustion, and that it then develops at constant pressure 2633 Cal., the water being liquid; or 2488 Cal., the water being supposed gaseous. The volume of oxygen employed is equal to 229 litres; the carbonic acid produced occupying 536 litres, the nitrogen 123 litres, and the water vapour (reduced volume) 324 litres.

2. This being granted, the total combustion by ammonium nitrate corresponds to the formula—

$$2[C_{24}H_{18}(NO_3H)_{11}O_9] + 41NO_3NH_4 = 48CO_2 + 111H_2O + 52N_2$$

Or 1640 grms. of nitrate for 1143 of gun-cotton; in all, 2783 grms. The substance, then, contains in 1 kgm. 589 grms. of nitrate and 411 grms. of gun-cotton, all the products being supposed dry and free from fixed ash. Sarrau and Vieille used 60 parts of nitrate to 40 parts of gun-cotton. The substances were triturated together, 24 parts of water having been previously added to the gun-cotton, then the whole dried at 60°. It was ascertained that the combustion of the mixture yielded only carbonic acid and nitrogen, these two gases being in the ratio of 54 : 46 volumes; the difference between which and the theoretical figures, or 52 : 48, corresponding to the slight

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deviation of the composition employed from the composition in equivalents.

In a miss-fire, on the contrary, combustion ceases to be total. The authors, for instance, have observed, out of 100 volumes of gas—

NO	29·5
CO	15·8
CO_2	24·8
H	2·9
N	2·7

3. The *heat liberated* by the total and regular reaction amounts, according to the calculation, to 3678 Cal. (water liquid), 3117·5 Cal. (water gaseous); or, for 1 kgm., 1321 Cal. (water liquid), or 1120 Cal. (water gaseous). Sarrau and Vieille actually found 1273 Cal. (water liquid) for a composition containing only 40 per cent. of gun-cotton instead of 41. The difference between the figure observed (1273) and the calculated figure (about 1288) does not exceed the limits of experimental error.

4. The *reduced volume of the gases* = 1116 litres (water liquid), 2399 litres (water gaseous); or, for 1 kgm., 401 litres (water liquid), and 862 litres (water gaseous). Sarrau and Vieille found 387 litres, with the composition containing 40 per cent. of gun-cotton instead of 41 per cent.

5. The permanent pressure $= \frac{401 \text{ atm.}}{n - 0{\cdot}36}$ under the ordinary reservations.

6. The theoretical pressure $= \frac{14900 \text{ atm.}}{n}$.

It is somewhat less than for gun-cotton.

Sarrau and Vieille actually found, with the composition containing 40 per cent. of gun-cotton, and by the crusher method—

Density of charge 0·2, P = 3270 kgm.
„ „ 0·3, P = 5320 kgm.

which would make for the density 1, 16358 and 17730; mean, 17000 kgm. approximately, a figure which is rather higher than 14900. But it is possible that it ought to be reduced to the half by a more exact estimation of the force of calibration (p. 23).

§ 6. Gun-cotton and Potassium Nitrate.

1. The total combustion of gun-cotton by potassium nitrate corresponds to the formula—

$$10[C_{24}H_{18}(NO_3H)_{11}O_9] + 82KNO_3 = 199CO_2 + 41K_2CO_3 + 145H_2O + 96N_2.$$

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Note further that during cooling the potassium carbonate is charged into bicarbonate, which gives finally—

$$158CO_2 + 82KHCO_3 + 104H_2O + 96N_2.$$

Or 828 grms. of nitrate for 1143 grms. of gun-cotton; in all, 1971 grms. The substance contains, therefore, for 1 kgm., 420 grms. of nitrate and 580 grms. of gun-cotton.

2. Sarrau and Vieille operated with equal weights, to assure total combustion. These proportions correspond practically with—

$$6[C_{24}H_{18}(NO_3H)_{11}O_9] + 68KNO_3 = 110CO_2 + 34K_2CO_3 + 87H_2O + 47O + 67N_2$$

or after cooling—

$$76CO_2 + 68KHCO_3 + 53H_2O + 67N_2 + 47O.$$

The authors have found, with high densities of charge (0·3 and 0·5), that a mixture of carbonic acid, nitrogen, and oxygen, in the following ratios of volume, is obtained—

52·3; 37·1; 10·7.

The formula gives— 54·9; 33·4; 11·7.

The difference shows that there probably exists a certain quantity of nitrite. With low densities of charge (0·023) the relative proportion by volume of carbonic acid increases (59·5), nitrogen diminishes (33·8), oxygen disappears, and carbonic oxide (5·0) and hydrogen (1·8) are obtained; the nitrite is necessarily here present in a considerable quantity. Lastly, in a combustion experiment at the atmospheric pressure, a condition comparable to a miss-fire, the authors obtained for 100 vol.—

NO	36·3
CO	29·5
CO_2	29·0
H	1·6
N	3·4

3. We shall give the calculations for the proportions (1) and (2), which correspond to total combustion. Equation (1) represents an exact combustion, without excess of oxygen; giving rise to a liberation of 1606 Cal. (initial formation of neutral carbonate and gaseous water), or of 1766 Cal. (bicarbonate, liquid water);[1] or for 1 kgm. of the substance, 815 Cal. or 891 Cal. Note that each molecule of liquefied water H_2O increases the heat by + 10 Cal. Each equivalent of carbonate changed into bicarbonate—

$$K_2CO_3 + CO_2H_2O \text{ liquid} = 2KHCO_3,$$

further increases the heat by + 12·4 Cal. If the water were gaseous to commence with, the increase would be + 17·4 Cal. Equation (2) represents a combustion with excess of nitrate and

[1] Neglecting the dissolving action of this water on the salt.

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consequently of oxygen. It corresponds to a liberation of 2240 Cal. (carbonate, gaseous water), or 2560 Cal. (bicarbonate, liquid water). Or for 1 kgm. of the substance, 980 Cal. or 1120 Cal. Sarrau and Vieille found 954 Cal. for a substance of this order; but, in reality, the combustion in their experiment did not give rise either to the total destruction of the nitrate, or, probably, to the integral and immediate change of the carbonate into bicarbonate.

4. The volume of the reduced gases will be, according to equation (1), 1062·5 litres (carbonate and gaseous water) or 728 litres (bicarbonate and liquid water); or, for 1 kgm., 475 litres or 271 litres.

Sarrau and Vieille found only 196 litres; a figure which is too low, for the reasons given above.

5. Owing to these considerable differences between the theoretical and the real equation, it appears useless to calculate the theoretical pressure of this powder. We will only mention that Sarrau and Vieille found, by the crusher process, operating on the product containing an excess of nitre—

Density of charge.	Pressure.
0·20...	1315 kgm.
0·30...	3100 „
0·40...	4900 „
0·50...	5520 „

values which are nearly the half of those given by pure gun-cotton or the same mixed with ammonium nitrate.

6. This is, moreover, what theory would enable us to foresee in a general way.

In fact, 1 kgm. of gun-cotton, decomposed under a high pressure, develops 859 litres and produces 1020 Cal. (water gaseous). On the other hand, 1 kgm. of gun-cotton mixed with ammonium nitrate develops 862 litres and produces 1120 Cal. (water gaseous). Whilst 1 kgm. of gun-cotton mixed with potassium nitrate can only develop 475 litres and produce 980 Cal.

The volume of the gases with the latter mixture is therefore nearly half that produced by the two other substances, the heat being slightly less. Consequently the pressures will fall to about the half for the same density of charge. Dissociation, moreover, will intervene to lower the initial pressure and moderate the fall of the successive pressures.

7. On the whole, theory does not show that the addition of potassium nitrate to gun-cotton, which is rather inconvenient to realise in practice, offers any very great advantages, except in the way of economising the gun-cotton, rendering expansion less abrupt and suppressing the carbonic oxide. The experiments which have been made with similar mixtures formed of various nitrocelluloses impregnated with potassium nitrate seem to point to this conclusion.

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8. The Faversham "Cotton Powder" consists of a mixture of equal weights of gun-cotton and barium nitrate. Gun-cotton may also be mixed with sodium nitrate, the hygroscopic properties of which lessen the risk of inflammation. But special detonators must then be employed. The relations by weight of total combustion would be 51·6 of gun-cotton to 48·4 of barium nitrate. The heat liberated is practically the same (pp. 4 and 134) as for an equivalent weight of potassium nitrate; but the barium nitrate mixture weighs 2223 grms. instead of 1971 grms., or one-eighth more.

The volume of the gases gives rise to the same relations, this volume being identical for equivalent weights (provided only the carbonate be neutral), but less at equal weights.

9. Schultze's powder, made from nitrated wood meal, will now be considered.

It is prepared from wood reduced to small grains, which are freed from resinous, nitrogenous, and incrusting matters by the following treatments. It is boiled for six to eight hours with sodium carbonate; washed, dried, and treated successively by steam, cold water, bleaching powder; then 16 parts of a mixture of nitric acid of 1·50 specific gravity, with twice its volume of concentrated sulphuric acid, is allowed to react for from two to three hours. In this way is obtained a substance nearly related by its composition to heptanitrocellulose—

$$C_{24}H_{26}(NO_3H)_7O_{13}.^1$$

In reality it is a mixture of several unequally nitrified products. It is washed in cold water, then in a weak solution of sodium carbonate. This done, the substance is steeped in a concentrated solution of potassium or barium nitrate, pure or mixed, and dried at 45°. The nitrate and the ligneous grains, which are impregnated beforehand with 20 to 25 per cent. of water, can again be incorporated under light edge runners. The composition of the final substance varies with the amount of the nitrates. The following is the result of some of the analyses:—

Nitrocellulose soluble in alcohol ether	13·1	58·0
" " insoluble " "	44·9	
Foreign matters soluble in alcohol		2·3
Potassium nitrate		6·2
Barium nitrate		30·0
Water		3·5
		100·0

Another sample—

Nitrocellulose	66·5
Barium nitrate	15·0
Potassium nitrate	15·0
Water	3·5
	100·0

[1] One grm. produces 166 cc. of nitric oxide by Schlœssing's process.

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The latter had as gravimetric density, 0·416.
Density taken with mercury, 0·944.

The substance gave 7300 granules to the gramme. It is as sensitive to shock as black powder, keeps well, decomposes towards 174°. It gives a light smoke which dissipates rapidly.

This powder has been much used for sporting purposes.

§ 7. Gun-cotton and Chlorate.

1. Some data may now be given regarding this mixture, the use of which, however, has been abandoned owing to the dangerous character of the chlorate powders.

2. The complete combustion corresponds with the following equations :—

$$6[C_{24}H_9(NO_3H)_{11}O_9] + 41KClO_3 = 144CO_2 + 87H_2O + 33N_2 + 41KCl.$$

It corresponds to the proportions, 1143 grms. of gun-cotton and 838 grms. of chlorate ; in all, 1981 grms. ; or, for 1 kgm. of the mixture, 577 grms. of gun-cotton and 423 grms. of chlorate.

3. It liberates 2708 Cal., the water being liquid,[1] and 2563 Cal., the water being gaseous ; or, for 1 kgm., 1367 Cal. (water liquid), or 1294 Cal. (water gaseous), figures which are somewhat higher than those for pure gun-cotton, but the volume of the gases is far less.

4. The volume of the reduced gases is 978·6 litres (water gaseous), or 653 litres (water liquid) ; or, for 1 kgm., 484·5 litres (gaseous water), or 323·5 litres (liquid water), figures lower by half than those for pure gun-cotton. They are likewise less than those for gun-cotton mixed with ammonium nitrate.

5. The permanent pressure is $\frac{323{\cdot}5 \text{ atm.}}{n - 0{\cdot}26}$, provided n be large enough for the carbonic acid not to be liquefied.

6. The theoretical pressure is $\frac{13175 \text{ atm.}}{n - 0{\cdot}08}$.

This number is less by a third than that for pure gun-cotton, and by an eighth than that for gun-cotton mixed with ammonium nitrate. The smallness of the gaseous volume would enable this inferiority to be anticipated. Gun-cotton mixed with potassium nitrate would alone yield volumes of nearly equal magnitude. Hence it will be seen that chlorated gun-cotton does not present, from the point of view of strength, the same advantages over the other varieties of gun-cotton, which have often been attributed to the chlorate powders. When we add that it is much more sensitive to shocks and friction, and therefore much more dangerous, it will be easy to understand the reasons which have led to the use of it being given up.

[1] Neglecting the action of this water on the potassium chloride.

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CHAPTER VIII.

PICRIC ACID AND PICRATES.

§ 1. Historical.

Trinitrophenol, otherwise termed picric acid, heated towards 300°, decomposes with a sudden explosion, and its salts behave in a similar manner. But the decomposition is complex, and only takes place at a temperature higher than that of nitroglycerin, when oxidising bodies, such as potassium nitrate or chlorate, are added. It occurs at a lower temperature than with the pure acids and salts, and yields simpler products. Powders of various natures are obtained in this way, some having as base picric acid and sodium nitrate (Borlinetto powders), others having as base potassium picrate associated either with potassium nitrate (Designolle powders) or chlorate (Fontaine powder); other powders again having as base ammonium picrate with potassium nitrate (Brugère powder and Abel powder). The chlorate powder has been proposed for torpedoes only, it being very dangerous. On the other hand, the powders formed with the nitrates can be employed in fire-arms, especially ammonium picrate powder, which has of late been greatly studied in France. We shall successively examine the picric acid, potassium picrate, and ammonium picrate powders.

§ 2. Picric Acid.

1. Picric acid is a yellow body, in laminated and friable crystals, having a bitter taste, very stable in itself, not easily soluble in water, but soluble in all other solvents.

When heated it melts, and can even be sublimed when very small quantities are operated upon. But if the quantity be at all considerable, or the acid be suddenly heated, it explodes very violently. This property has occasioned serious accidents. For instance, it has happened that experimenters have been injured by throwing powdered picric acid into a furnace from a

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flask to show its explosion, the latter having been propagated backwards along the trail of dust up to the principal mass.

2. The formula for picric acid is $C_6H_3(NO_2)_3O$, its equivalent 229.

3. Its heat of formation from the elements (p. 277)—

$$C_6 \text{ (diamond)} + H_3 + N_3 + O_7 = C_6H_3N_3O_7 + 49{\cdot}1.$$

This body hardly contains more than half the oxygen necessary for its complete combustion.

4. Its heat of total combustion by free oxygen—

$$2[C_6H_3(NO_2)_3O] + O_{13} = 12CO_2 + 3H_{20} + 3N_2,$$

is equal to + 618·4 Cal. (water liquid), according to the results of the experiments of Sarrau and Vieille.

5. The equation representing its explosive decomposition has not been studied. Admitting provisionally the following—

$$2[C_6H_3(NO_2)_3O] = 3CO_2 + 8CO + C + 6H + 6N,$$

the heat liberated would be + 130·6 Cal., or 570 Cal. per kilogramme.

6. The reduced volume of the gases would be 190 litres per equivalent, or 829 litres per kilogramme.

7. This figure divided by n, or $\frac{829 \text{ atm.}}{n}$, practically represents the permanent pressure, owing to the small volume occupied by the carbon, with the usual exception of the liquefaction of the carbonic acid.

8. Lastly, the theoretical pressure $= \frac{10942 \text{ atm.}}{n}$. These values are only given with all due reserve.

9. To obtain a total combustion of picric acid, recourse must be had to a complementary oxidising agent—nitrate, chlorate, etc. It has been proposed, for instance, to mix picric acid (10 parts) with sodium nitrate (10 parts) and potassium bichromate (8·3 parts). These proportions would furnish a third of oxygen in excess of the necessary proportion.

But it is doubtful whether this powder has ever been prepared on a large scale or kept. In fact, the mechanical mixture of bodies of this nature can only be executed without danger on the condition of wetting the pulverised substances before incorporating them under the millstone or otherwise. Now, as soon as water intervenes, the picric acid displaces the nitric acid of the nitrates, even in the cold, and this volatile acid disappears wholly or partly during the drying in the stove. This circumstance hardly permits of employing free picric acid in the manufacture of powders.

An analogous reaction renders its mixture with potassium chlorate particularly dangerous.

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§ 3. Picrate Potassium.

1. Potassium picrate,

$$C_6H_2K(NO_2)_3O,$$

crystallises in long orange-yellow needles, very slightly voluble in water.

2. It explodes, when heated above 300°, much more violently than picric acid. It also explodes by contact with an ignited body, which renders it still more dangerous than black powder. In the dry state its fine and light dust takes fire at a distance, and may cause the whole mass from which it emanates to explode. Operators have been wounded in public lectures by throwing upon lighted coals potassium picrate contained in a flask. This kind of accident is even more to be feared with potassium picrate than with picric acid. The catastrophe in the Place de la Sorbonne (1869) appears due to this property. Potassium picrate is sensitive to shock, and even much more so than picric acid. The addition of 15 per cent. of water deprives it of this sensitiveness. Potassium picrate does not contain enough oxygen to produce complete combustion. Hence the necessity for mixing it with potassium nitrate or chlorate.

3. Its equivalent is 267.

4. Its heat of formation from the elements—

$$C_6 \text{ (diamond)} + H_2 + K + N_3 + O_7 = C_6H_2K(NO_2)_3O,$$

is equal to + 117·5 Cal., according to the data of Sarrau and Vieille.

5. The heat of total combustion by free oxygen—

$$2[C_6H_2K(NO_2)_3O] + O_{12} = 2KHCO_3\,10CO_2 + H_2O + 6N,$$

amounts to 619·7 Cal. (potassium bicarbonate and liquid water). The explosive decomposition of potassium picrate yields products which vary with the conditions, as is generally speaking the case with bodies which do not contain a sufficient quantity of oxygen to produce complete combustion (p. 7).

Sarrau and Vieille have studied this decomposition minutely. The following are the results obtained by them,[1] with various densities of charge, per 100 vols.—

	Densities of charge.		
	0·023 lit.	0·3 lit.	0·5 lit.
HCy	1·98	0·32	0·31
CO_2	10·66	13·37	20·48
CO	62·10	59·42	50·88
CH_4	0·17	2·38	5·39
H	10·31	6·77	2·68
N	16·88	17·74	18·26
Volume of gases disengaged per 1 kgm.,	574·1,		557·9.

[1] "Comptes rendus des séances de l'Académie des Sciences," tom. xciii. p. 6.

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6. The solid residuum is formed of potassium carbonate and cyanide, with a trace of carbon. The proportion of potassium changed to cyanide, in 100 parts, amounted respectively to 29·8, 34·7, 24·3. At the density 0·5, the reaction approximates to the following formula:—

$$16C_6H_2K(NO_2)_3O = 4KCN + 6K_2CO_3 + 21CO_2 + 52CO + 44N + 6CH_4 + 8H + 7C.$$

It tends towards $4CH_4 + 5C$; that is to say, the methane is formed in an increasing quantity, according as the density augments. On the contrary, the methane tends to disappears for low densities.

7. *Heat of decomposition.* The formula given above would correspond to + 208·4 Cal. for 1 equiv. of picrate decomposed, or 781·2 Cal. for 1 kgm.

8. *Volume of the gases.* It would yield 146·5 litres (reduced volume) of gases per equiv., or 549 litres for 1 kgm.

9. The theoretical pressure $= \frac{5600 \text{ atm.}}{n - 0{\cdot}14}$.

Sarrau and Vieille found 6700 kgm. at low densities of charge, such as 0·023.

It has been seen that for high densities the gaseous volume found tends to approach the theoretical figure. Now, at these high densities the ratio $\frac{P}{n}$ has been found by the same authors at nearly 12,000 kgm., a figure which should be corrected according to their recent experiments (p. 23). These point to about the half, or 6600 kgm., a value near the theoretical figure, which would correspond, for $n = 1$, to 6700 kgm. It will further be seen that it is greatly lower than the pressures developed by nitroglycerin, or by gun-cotton, for the same density of charge (p. 425). This is, in fact, as it should be, according to theory, the heat liberated being less, weight for weight, as well as the volume of the gases.

Potassium picrate, therefore, does not offer the advantages which had been anticipated from it at first, from the abruptness of its explosive effects.

§ 4. Potassium Picrate with Nitrate.

1. The total combustion of potassium picrate by potassium nitrate corresponds to the following formula:—

$$5C_6H_2K(NO_2)_3O + 13KNO_3 = 9K_2CO_3 + 21CO_2 + 5H_2O + 28N.^1$$

2. The total weight of the substance in equivalents is 267 grms. of picrate and 263 grms. of nitrate; in all, 530 grms. For

[1] The slow formation of 2 equiv. of bicarbonate is here neglected.

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1 kgm. both bodies are nearly in equal weights, 504 grms. of picrate to 496 grms. of nitrate. This composition is that of torpedo powders.

3. The heat liberated amounts to + 538·0 Cal. (water liquid), or + 528·2 Cal. (water gaseous); or, for 1 kgm., 1015 Cal., or 997 Cal.

4. The reduced volume of the gases = 170 litres (water gaseous), or 116 litres (liquid water and bicarbonate); or, for 1 kgm., 326 litres, or 246 litres.

5. The theoretical pressure is $\frac{6320 \text{ atm.}}{n - 0{\cdot}21}$; it does not greatly differ from the value for pure potassium picrate.

6. The potassium picrate powders proposed for cannons and guns have a different composition. The amount of picrate has been diminished in order to reduce its shattering properties, and it has been replaced by carbon; for cannons, 9 parts by weight of picrate, 80 of nitre; for guns, 23 parts of picrate, 69 of nitre, 8 of carbon, etc.

§ 5. Potassium Picrate with Chlorate.

1. The total combustion of potassium picrate by potassium chlorate corresponds to the formula—

$$6C_6H_2K(NO_2)_3O + 13KClO_3 = 3K_2CO_3 + 33CO_2 + 6H_2O + 18N + 13KCl,$$

or rather

$$6KHCO_3 + 30CO_2 + 3H_2O + 18N + 13KCl.$$

2. The equivalent weight is 267 grms. of picrate to 265·7 of chlorate; in all, 532·7 grms.

For 1 kgm., 502 grms. of picrate and 498 grms. of chlorate; that is to say, nearly equal weights. The composition is, moreover, very nearly the same by weight for the nitrated and the chlorated powders, owing to a numerical coincidence in the equivalents.

3. The heat liberated will be 622·2 Cal. (gaseous water and carbonate), or 647·6 (liquid water and bicarbonate); or, for 1 kgm., 1168 Cal., or 1214 Cal.

4. The reduced volume of the gases, 178·6 litres (gaseous water), or 145 litres (liquid water, bicarbonate); or, for 1 kgm., 335 litres, or 272 litres.

5. The permanent pressure $= \frac{272 \text{ atm.}}{n - 0{\cdot}21}$, with the usual exception.

6. The theoretical pressure, $\frac{8200 \text{ atm.}}{n - 0{\cdot}21}$, is about a third greater than that of nitrated picrate and that of pure picrate. But it hardly reaches half of that of dynamite or gun-cotton.

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Hence it will be seen that "chlorated" picrate does not bear out, by an exceptional strength, the hopes which the vivacity of its explosion had given rise to at the outset. It therefore does not compensate in this direction for the considerable dangers which result from its great sensitiveness to shock, friction, and inflammation, as well as the easy propagation of the latter by dust trails. Its use, therefore, seems to be almost abandoned.

§ 6. Ammonium Picrate.

1. This is an orange-yellow salt, in needles, less hard than potassium picrate. It is far less sensitive to shock. Ignited in the open air it burns like a resin, with a smoky flame. It has been used in pyrotechny as a fusing substance. However, when burnt at a high density of charge, or in a confined space, from which the gases only escape by a small orifice, its combustion may change into detonation.

2. Its formula is—

$$C_6H_2(NH_4)(NO_2)_3O\,;$$

its equivalent, 246.

3. Its heat of formation from the elements—

$$C_6 + H_6 + N_4 + O_7 = C_6H_6N_4O_7,$$

is equal to + 80·1 Cal.; or, for 1 kgm., 326 Cal.

4. Its total combustion needs an excess of oxygen—

$$C_6H_6N_4O_7 + O_8 = 6CO_2 + 3H_2O + 2N_2,$$

and liberates + 690·4 Cal. (liquid water), or + 660·4 Cal. (gaseous water).

5. The equation of the explosive decomposition has not been studied.

6. Only the combustion by a combustive agent, such as potassium nitrate, will be examined—

$$5C_6H_6N_4O_7 + 16KNO_3 = 8K_2CO_3 + 22CO_2 + 15H_2O + 36N,$$

or

$$16KHCO_3 + 14CO_2 + 7H_2O + 36N$$

after cooling.

The total weight is here 569·5 grms. per 1 kgm.; viz., 568 grms. of saltpetre and 432 grms. of picrate.

The heat liberated by the combustion of "nitrated" ammonium picrate amounts to + 701 Cal. (liquid water, bicarbonate), or to + 631·5 Cal. (gaseous water); or, per 1 kgm., 1231 Cal., or 1109 Cal.

7. The reduced volume of the gases = 245·5 litres (gaseous water), or 174 litres (liquid water, bicarbonate), which makes per 1 kgm. 431 litres, or 305 litres.

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8. The permanent pressure $= \frac{305 \text{ atm.}}{n = 0{\cdot}17}$, with the usual exception.

9. The theoretical pressure $= \frac{9050 \text{ atm.}}{n - 0{\cdot}17}$.

It is higher than that of potassium picrate, whether pure or mixed with potassium chlorate or nitrate.

10. The Brugère powder is, in fact, formed of ammonium picrate and potassium nitrate. It contains 54 parts of picrate and 46 of saltpetre. Here combustion is not total, and the true reaction is therefore imperfectly known.

This powder is only slightly hygroscopic: it is stable, and makes little smoke. Its strength is double that of black powder weight for weight.

11. On account of its fusing properties, ammonium picrate can also be employed in fireworks.

For example, this salt mixed with barium nitrate gives green fires.

Designolle powder	Ammonium picrate	48
	Barium nitrate	52
Brugère powder	Ammonium picrate	25
	Barium picrate	67
	Sulphur	8

Mixed with strontium nitrate it gives red fires.

Ammonium picrate	54
Strontium nitrate	46

None of these proportions correspond to total combustion.

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CHAPTER IX.

DIAZO COMPOUNDS AND OTHERS.

§ 1. Summary.

We shall give in this chapter the observations and calculations relative to various explosive compounds, such as mercury fulminate and diazobenzene nitrate, both belonging to the group of diazo compounds, the acid mixtures formed of nitric acid associated with an organic compound, which is generally already nitrified, the perchloric ethers and mercury and silver oxalates. This list might be made much longer in theory (see p. 368 and the following), but experimental data and practical applications would be wanting.

§ 2. Mercury Fulminate.

1. The analysis and mode of decomposition of this body have been given (p. 297)—

$$C_2N_2HgO_2 = 2CO + Hg + N_2.$$

2. This reaction liberates + 114·5 Cal. at constant pressure for 284 grms.; the mercury being supposed gaseous, + 99·1 Cal.; or, for 1 kgm., 463 Cal. or 349 Cal.

3. The formation from the elements absorbs − 62·9 Cal. for 284 grm., or − 221·5 Cal. for 1 kgm.

4. The total combustion by free oxygen—

$$C_2N_2HgO_2 + O_2 = 2CO_2 + Hg + N_2, \text{ liberates } + 250{\cdot}9 \text{ Cal.},$$

or, the mercury being gaseous, + 235·5 Cal.

5. The density is equal to 4·43.

6. Pure fulminate may be kept for an indefinite length of time. Water does not affect it. It explodes at 187°, and also on contact with an ignited body.

It is very sensitive to shock and friction, even that of wood upon wood. When used in a cannon, it bursts it, without the projectile having time to displace itself. However, it may be

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employed for discharging bullets in saloon arms. If placed in a shell, and the latter can be projected by the aid of some artifice of progressive expansion, the shell bursts at the striking point, owing to the shock and heating resulting from the sudden stoppage of the projectile. A hollow projectile is broken by fulminate into a multitude of small fragments, much more numerous than those produced by powder, but which are not as widely scattered.

Its inflammation is so sudden that it scatters black powder on which it is placed without igniting it; but it is sufficient to place it in an envelope, however weak, for ignition to take place. The more resisting the envelope the more violent is the shock, a circumstance which plays an important part in caps and detonators.

The presence of 30 per cent. of water prevents the decomposition of finely powdered fulminate by friction or shock. With 10 per cent. of water, it decomposes without explosion; with 5 per cent., the explosion does not extend beyond the part struck. But these results are only strictly true for small quantities of the substance, and it would be dangerous to attach too much importance to them.

Moist fulminate slowly decomposes on contact with the oxidisable metals.

7. The reduced volume of the gases produced by the decomposition is 66·96 litres per 284 grms., or 235·6 litres per 1 kgm.

If the mercury be supposed in the gaseous state, at a suitable temperature t, we shall have 89·28 litres $(1 + at)$ per 1 equiv., or per 1 kgm., 314·1 litres $(1 + at)$.

8. The permanent pressure $= \frac{235{\cdot}6 \text{ atm.}}{n - 0{\cdot}05}$.

9. The theoretical pressure $= \frac{6280 \text{ atm.}}{n}$.

The experiments which the author made with the crusher, in common with M. Vieille, gave—

Density of charge		0·1	...	...	...	480 kgm.
„	„	0·2	...	...	...	1730 „
„	„	0·3	...	...	...	2700 „

We should, therefore, have for high densities about $\frac{9000 \text{ atm.}}{n}$.

But these figures should be reduced, in accordance with a more exact estimation of the force of calibration (see p. 23). The corrected calculation gives results very closely agreeing with theory (p. 27), and leads to a specific pressure equal to $\frac{6200 \text{ kgm.}}{n}$. At the density 4·43, that is to say, the fulminate exploding in its own volume, we should have, therefore,

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28,750 kgm. according to the theoretical formula, or 27,470 kgm. according to the indications of the crusher—values higher than those of all known explosives. In fact, nitroglycerin gave only 12,376 kgm., and gun-cotton 9825 kgm.

It is the immensity of this pressure, combined with its sudden development, which explains the part played by mercury fulminate as priming.

Silver fulminate presents very similar properties; but it is much more sensitive, and therefore more dangerous.

§ 3. Mercury Fulminate mixed with Nitrate.

1. Suppose, now, *mercury fulminate mixed with potassium nitrate*, the mixture corresponds to the formula—

$$6C_2N_2O_2Hg + 5KNO_3;$$

that is to say, 284 grms. of fulminate to 84·2 of saltpetre; in all, 368·2 grms. Or for 1 kgm. of the mixture, 229 grms. of saltpetre and 771 grms. of fulminate.

In practice a third of saltpetre, that is, an excess, is employed. Antimony and lead sulphides are also added.

2. The heat liberated is + 224 Cal., the mercury liquid; + 209·6 Cal., the mercury gaseous; or, for 1 kgm., + 609 Cal. or + 567 Cal.

3. The reduced volume of the gases = 64·9 litres, or (gaseous mercury) 87·2 litres for 1 equiv.; or, for 1 kgm., 176 litres or 257 litres.

4. The permanent pressure $= \frac{176 \text{ atm.}}{n - 0{\cdot}12}$, with the usual reservation.

5. The theoretical pressure $= \frac{4380 \text{ atm.}}{n - 0{\cdot}12}$.

It will be seen that it is less by about a third than the pressure corresponding to pure fulminate. Further, the presence of the nitrate diminishes the rapidity of inflammation and the violence of the shock. On the other hand, it gives more expansion to the flame.

§ 4. Mercury Fulminate mixed with Chlorate.

1. The reaction is the following (exact combustion)—

$$3C_2N_2O_2Hg + 2KClO_3 = 6CO_2 + 3N_2 + 3Hg + 2KCl;$$

that is to say, 284 grms. of fulminate to 81·7 of chlorate; in all, 356·7 grms.; or, for 1 kgm. of the mixture, 223 grms. of chlorate and 777 grms. of fulminate.

2. The heat liberated is + 258·2 Cal. for 1 equivalent, or

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+ 242·8 Cal. (gaseous mercury); or, for 1 kgm., 706 Cal., or 663 Cal.

3. The reduced volume of the gases = 67 litres, or 89·2 litres (gaseous mercury); or, for 1 kgm., 183 litres, or 244 litres.

4. The permanent pressure = $\frac{183 \text{ atm.}}{n - 0{\cdot}11}$ with the usual reservation.

5. The theoretical pressure = $\frac{6830 \text{ atm.}}{n - 0{\cdot}11}$.

It is very nearly the same as that of pure fulminate. Potassium chloride lessens the effects of the shock; but potassium chlorate renders the mixture very sensitive. Accidents, therefore, frequently occur in factories when this mixture is being prepared.

§ 5. Diazobenzene Nitrate.

1. The properties and analysis of this body, as well as the study of its explosive decomposition, have been set forth (p. 291). We shall only repeat the following figures.

The formula is—

$$C_6H_4N_2NO_3H = 167 \text{ grms.}$$

2. The formation from the elements absorbs − 47·4 Cal.

3. The total combustion—

$$2C_6H_4N_2NO_3H + 23O = 12CO_2 + 5H_2O + 6N,$$

liberates + 782·9 Cal. at constant pressure (liquid water). No attempt has been made to study the effects of the combustion of diazobenzene by the oxidising bodies. The mixture with these bodies would, moreover, present great difficulties, owing to the sensitiveness of the dry substance and its immediate decomposition by water.

4. The explosive decomposition yields complex products, which vary with the conditions. They have been noticed (p. 293).

5. *Heat liberated.* The decomposition having been effected by the incandescence of a platinum wire, at a low density of charge, it liberated + 114·8 Cal. at constant volume for 1 equiv., or 687·7 Cal. for 1 kgm.

6. *Gaseous volume.* There was produced at the same time 136·6 litres of gas (reduced volume) for 1 equiv., or 817·7 litres for 1 kgm.

7. The theoretical pressure = $\frac{10400 \text{ atm.}}{n - 0{\cdot}05}$. It is higher than that of the fulminate at the unit of weight, and approaches that of the most powerful substances.

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8. Let us compare these theoretical results with the experimental measurement of the pressures. M. Vieille and the author obtained with a crusher the following figures :—

Density of charge.		Weight of the charge.		Pressures in kgms. per square centimetre.
0·1	...	2·37 grms.	...	990 kgm.
0·2	...	4·74 „	...	2317 „
0·3	...	7·11 „	...	4581 „

In the last experiment made with diazobenzene nitrate, this body filled the whole of the vacant space, and the steel tube was cracked. This points to local effects, which may have slightly affected the results. The recent researches of Sarrau and Vieille on the calibration of the "crushers" tend to reduce by half the absolute value of the pressures for substances having so sudden an explosion, but without changing the relations.

In any case, the pressures of diazobenzene nitrate are far higher, actually and theoretically, for the same density of charge, than those developed by the explosion of mercury fulminate. On the contrary, the fulminate exploding in its own volume would develop a far greater pressure (28750 kgm., instead of 7500 kgm.), owing to its great density.

The great activity of diazobenzene nitrate, in any case, renders it more dangerous.

§ 6. Nitric Acid associated with an Organic Compound.

1. It has been seen in Chapter III. (p. 396), how the liquefied oxygenated gases, especially nitrogen monoxide and nitric peroxide, when mixed with combustible liquids, form explosive substances of a very special character. It has been proposed to prepare similar substances by mixing nitric acid with combustible organic substances. In case of need the mixture may be made on the spot, the ingredients being separately conveyed; it is exploded by a fulminate cap. This is the principle of Sprengel's acid explosive. In practice, the substances capable of being mixed with nitric acid are few in number, owing to the violent oxidising action exerted by this acid on the greater number of organic substances. Few liquids can be mixed with it without being attacked, and the pastes formed by imbibition are also subject to reaction.

In fact, only two mixtures of this kind have been employed, or rather, specially prepared—the mixture of picric acid (solid) and nitric acid, which forms a paste; and the mixture of nitrobenzene and the same acid, bodies which dissolve each other reciprocally. It will be seen that it is two already nitrified bodies which serve as base to the mixtures; further, that the second would soon be transformed into crystallised dinitro-

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benzene. We will now give the theoretical calculations for the combustion of these two mixtures, including dinitrobenzene.

§ 7. Nitric Acid and Picric Acid.

1. The reaction corresponding to total combustion is,

$$5C_6H_3(NO_2)_3O + 13HNO_3 = 30CO_2 + 14H_2O + 28N.$$

2. The proportions by weight are, 229 grms. of picric acid to 164 grms. of nitric acid; in all, 393 grms.; or, per kilogramme, 583 grm. of picric acid and 417 grms. of nitric acid.

3. The heat liberated will be, for 1 equiv., 318 Cal. (liquid water), or 290 Cal. (gaseous water); or, for 1 kgm., 809 litres, or 738 Cal.

4. The reduced volume of the gases, for 1 equiv., 500 litres, or 659 litres.

5. The permanent pressure $= \frac{500 \text{ atm.}}{n - 0{\cdot}13}$, with the usual reservation of the limit of liquefaction of carbonic acid.

6. The theoretical pressure $= \frac{9450 \text{ atm.}}{n}$.

No experiment has been made with the object of directly measuring the heat, the volume of the gases, or the pressure; a remark which is equally applicable to the following mixtures.

§ 8. Nitric Acid and Nitrobenzene.

1. The reaction of total combustion is—

$$C_6H_5NO_2 + 5HNO_3 = 6CO_2 + 5H_2O + 6N.$$

2. The proportions by weight are, 123 grms. nitrobenzene to 315 grms. nitric acid; in all, 438 grms.; or, for 1 kgm., 719 grms. acid and 281 grms. nitrobenzene. It will be borne in mind that the nitrobenzene is liquid.

3. The heat liberated[1] will be, for 1 equiv., 415 Cal. (liquid water), or 365 Cal. (gaseous water); or, for 1 kgm., 947 Cal., or 834 Cal.

4. The reduced volume of the gases, for 1 equiv., 201 litres (liquid water), 373 litres (gaseous water); or, for 1 kgm., 459 litres, or 714 litres.

5. The permanent pressure $= \frac{459 \text{ atm.}}{n - 0{\cdot}21}$, with the usual reservation.

6. The theoretical pressure $= \frac{10700 \text{ atm.}}{n}$.

[1] The previous solution of the nitrobenzene in the acid is here neglected.

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§ 9. Nitric Acid and Dinitrobenzene.

1. The reaction of total combustion is—

$$C_6H_4N_2O_4 + 4NO_3H = 6CO_2 + 4H_2O + 3N_2.$$

2. The proportions by weight are, 168 grms. of dinitrobenzene to 252 grms. of acid; in all, 420 grms.; or, for 1 kgm., 400 grms. of dinitrobenzene and 600 grms. of acid. Note that the dinitrobenzene is crystallised.

3. The heat liberated will be, for 1 equiv., 387·4 Cal. (liquid water), or 347·4 Cal. (gaseous water); or, for 1 kgm., 899 Cal., or 827 Cal.

4. The reduced volume of the gases, for 1 equiv., 201 litres (liquid water), or 290 litres (gaseous water); or, for 1 kgm., 479 litres, or 690 litres.

5. The permanent pressure $= \frac{479 \text{ atm.}}{n - 0{\cdot}18}$.

6. The theoretical pressure $= \frac{10800 \text{ atm.}}{n}$, with the usual reservation.

It is nearly identical with that of nitrobenzene. This is as it should be, the heat liberated and the reduced gaseous volume being nearly the same for equal weights. With picric acid the difference is also slight. On the whole, all these mixtures are very inferior in theory to nitroglycerin or gun-cotton. The corrosive properties of nitric acid must, moreover, render difficult the transport of mixtures made beforehand. Lastly, the stability of such mixtures is more than doubtful. But they have this advantage, that they can be prepared on the spot and instantaneously.

§ 10. Perchloric Ethers.

1. The ethers of the highly oxygenated acids are probably explosive, but the only ones which have so far been prepared are the perchloric ethers. These are, in fact, eminently explosive bodies. The thermal and mechanical properties of methyl-perchloric ether, the only one corresponding to a total combustion among the ethers of monatomic alcohols, will be given.

2. The formula for methylperchloric ether is the following:—

$$CH_2(ClO_4H).$$

It corresponds to the equivalent 114·5.

3. The explosive decomposition will be—

$$CH_2(ClO_4H) = CO_2 + H_2O + HCl + O.$$

It will be seen that it sets free an excess of oxygen, like nitroglycerin and nitromannite.

4. The heat of formation of methylperchloric ether, from the

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elements, may be calculated, granting the formation of this ether from the acid and alcohol, both dilute.

$$CH_4O \text{ (dilute)} + ClO_4H \text{ (dilute)} = CH_3(ClO_4H) \text{ (dilute)} + H_2O$$
$$\text{absorbs} - 2{\cdot}0 \text{ Cal.},$$

a value found in general for organic oxacid ethers, and even for nitric ether itself.

We further have—

$C + H_4 + O$ + water = CH_4O (dissolved)	+ 64·0
$Cl + O_4 + H$ + water = ClO_4H (dilute)	+ 4·9
Reaction	− 2·0
	+ 66·9

Supposing the solution of the ether in the water to have liberated + 2·0, the formation of the pure ether then corresponds to + 65 Cal.

Now, the formation of H_2O produces + 69·0. We finally obtain—

$$C + H_3 + O_4 + Cl = CH_3(ClO_4H) \text{ (dilute)} - 4{\cdot}0 \text{ Cal.},$$

approximately.

5. The explosive decomposition will liberate[1] + 175 Cal. (gaseous water); or, for 1 kgm., + 1529 Cal.

6. It will produce 78·1 litres, or, for 1 kgm., 682 litres.

7. The permanent pressure would be calculated from this figure if reaction did not take place between water and the acid during cooling (see note).

8. Theoretical pressure $= \frac{17730 \text{ atm.}}{n}$.

9. From these numbers the heat liberated is nearly that of nitroglycerin (1480 Cal. for 1 kgm. and gaseous water). The gaseous volume is also nearly the same.

It is therefore easy to understand that the theoretical pressure must also be nearly the same as that of nitroglycerin. We should have a still more powerful effect by mixing 3 equiv. of methylperchloric ether with 1 equiv. of ethylperchloric ether, so as to obtain an exact combustion of both ethers. On the whole, the explosive properties of the perchloric ethers correspond to those of nitroglycerin and the most powerful substances. It is this that has led the author to mention here this class of compounds.

§ 11. Silver Oxalate.

1. It has been shown (p. 366) that this compound is explosive, and explodes by shock, or heating, towards 130°. It is even a shattering body.

[1] HCl and H_2O being supposed separated from each other in the gaseous state. In reality there will be a partial reaction during cooling with formation of hydrate and corresponding liberation of heat.

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2. The following reaction—

$$C_2AgO_4 = 2CO_2 + Ag_2$$

corresponds to 304 grms. of the substance.

3. It liberates + 29·5 Cal. for 1 equiv., or + 97 Cal. for 1 kgm.

4. The reduced volume of the gases is 44·6 litres for 1 equiv., or 114 litres for 1 kgm.

5. The permanent pressure $= \frac{114 \text{ atm.}}{n - 0{\cdot}06}$, with the usual reservation.

6. The theoretical pressure $= \frac{712 \text{ atm.}}{n - 0{\cdot}06}$.

This pressure is much less than that of the explosives hitherto examined. However, owing to the great density of the salt, it would be nearly quadrupled, if the latter exploded in its own volume, which accounts for the shattering character of the compound.

§ 12. Mercury Oxalate.

1. This is a white, heavy, hard powder, which does not explode by shock, but which explodes feebly by heating.

2. The reaction—

$$C_2HgO_4 = 2CO_2 + Hg,$$

corresponds to 288 grms. of matter.

3. It liberates + 17·3 Cal. per equivalent (liquid mercury), or + 1·9 Cal. (gaseous mercary); or, for 1 kgm., + 60 Cal., or 6·6 Cal.

4. The reduced volume of the gases is, for 1 equiv., 44·6 litres (liquid mercury), or 66·9 litres (gaseous mercury); or, for 1 kgm., 155 litres, or 227 litres.

5. The permanent pressure $= \frac{155 \text{ atm.}}{n - 0{\cdot}05}$, with the usual reservation.

6. Theoretical presure $= \frac{300 \text{ atm.}}{n}$.

This pressure is very small compared with the other explosive substances, which explains why mercury oxalate explodes so feebly, and why the mixture of mercury oxalate with the fulminate, which is produced when the manufacture is defective, greatly lessens the properties of the fulminate.

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CHAPTER X.

POWDERS WITH A NITRATE BASE.

§ 1.

1. BLACK powder consists of a mixture of saltpetre, sulphur, and charcoal. According to the relative proportions of these three ingredients, there is obtained—*service powder*, in which the greatest possible strength is sought for; *sporting powder*, in which facility of inflammation and combustion are aimed at; and *blasting powder*, for which the most copious production of gas is desired. Even the proportions of the ingredients of each of these powders vary with different nations between very wide limits.

Few substances have been more studied than powders of this kind, and there is a copious literature on this subject. It is not intended to give here a detailed examination of them, which may be found in a more complete manner in the "Treatise" by Piobert, in the "Traité sur la Poudre, par Upmann et Meyer" (traduit et augmenté par Desortiaux), as well as the long and important pamphlets written by Bunsen and Schisckhoff, Linck, Karolyi, and especially by Noble and Abel, Sarrau, Vieille, Sébert, etc. Here we shall confine ourselves to examining the various powders from the point of view of the chemical reactions developed by their combustion, as well as the heat liberated, and the volume of the gases produced by these reactions. The results of theory with those of experiment will be compared, as far as is permitted, by the following circumstances, which are difficult to introduce into a precise calculation:—

1st. The charcoal employed is not pure carbon. It contains only 75 or 80 per cent. of this element, 2 per cent. of hydrogen, 1 or 2 per cent. of ash, and 15 or 20 per cent. of oxygen.

2nd. Powder contains a little moisture, the quantity of which varies, being, however, generally nearly 1 per cent.

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3rd. The mixture of sulphur, saltpetre, and charcoal is never absolutely intimate, and undergoes continual variations during the course of the operations.

4th. The combustion is never total, small quantities of nitre and sulphur principally escaping the reaction owing to the lack of homogeneousness. The saltpetre itself, under the influence of the high temperature of explosion, tends at first to yield the nitrites, then more and more stable compounds (hyponitrites, potassium peroxide, etc.) still imperfectly known.

5th. The metallic vessels (iron, copper), in which the operations are carried out, are attacked, with the formation of metallic sulphides, single and double sulphides resulting from the association of the former with potassium sulphide. Nevertheless the theoretical calculations, however imperfect their relation to practical conditions may be, offer the advantage of indicating the maximum limit of the effects which we may hope to attain, and the direction which should be given to experimental inquiry for this end. In order to explain more clearly the chemical phenomena, the fresh experiments will be given which the author has lately made on various questions relating to the theory of the reactions developed during the explosion of service powder, such as the reactions between the sulphur, the carbon, their oxides and salts (§ 2). The decomposition by heat of the alkaline sulphides (§ 3). The decomposition by heat of the alkaline hyposulphites (§ 4). The measurement of the heat of combustion of the charcoal employed in the manufacture of powder (§ 5).

These preliminary notions having been gained, we shall study—

1st. Powders corresponding to an exact combustion (§ 6).

2nd. Powders with an excess of combustible, such as service powder properly so called, sporting and blasting powder (§ 7).

3rd. Powders formed of nitrates other than potassium, which are employed for industrial purposes in particular cases (§ 8).

§ 2. Reactions between Sulphur, Carbon, their Oxides and Salts.

1. The study of the products of the explosion of powder led the author to make some observations on the reciprocal action of sulphur, carbon, their oxides and salts. The operations were, in some cases, carried out by means of the electric spark, and in others by means of a red heat. In both cases there are foreign energies which intervene in the chemical actions properly so called, energies developed by electricity or heating, especially successive decompositions, dissociations, and changes of molecular states (polymerised carbon changed into gaseous

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carbon, gaseous sulphur reduced to its normal molecular weight, instead of sulphur of triple density volatilisable towards 448°).

It may be first noted that sulphur burning in dry oxygen produces sulphurous acid, mixed with a considerable proportion of anhydrous sulphuric acid. Sulphur vapour directed upon charcoal at a red heat combines with it, producing carbon sulphide.

Carbon burnt in oxygen produces carbonic acid, always mixed with a little carbonic oxide.

Carbonic acid directed upon red-hot charcoal is changed into carbonic oxide; but the transformation is never complete.

2. *Decomposition of the sulphurous gas.* A series of electric sparks decompose sulphurous acid gas into sulphur and sulphuric acid (Buff and Hoffman)—

$$3SO_2 = 2SO_3 + S.$$

Operating in a sealed tube without mercury, with platinum electrodes, several hours are needed to decompose the half of the gas, and decomposition ceases at a certain point, as was observed by Deville. It does not yield free oxygen, but a portion of the sulphur unites with the platinum.

The greater portion of the sulphur forms with anhydrous sulphuric acid a special viscid compound, which, moreover, absorbs a certain quantity of sulphurous gas. This compound is the real medium of the reaction. Being inversely decomposable, the tension of sulphurous and sulphuric gases which it gives off limits the reaction.

3. *Decomposition of the carbonic oxide.* Carbonic oxide under the influence of the spark, or even of a white heat, partly decomposes into carbon and carbonic acid—

$$2CO = CO_2 + C.$$

But the reaction is limited to a few thousandth parts. It was found that it takes place at a bright red heat, and even at the temperature of the softening of glass. The carbon is deposited at the point where the porcelain tube issues from the furnace, and undergoes a lowering of temperature, even without having recourse to the artifice of the hot and cold tube. It may be still better shown by placing fragments of pumice-stone in this region of the tube. A trace of carbonic acid produced at the same time may be observed in the gases collected by adopting certain precautions.

Though so slight and inappreciable, this reaction is, nevertheless, of great importance; for it intervenes, together with the dissociation of the carbonic gas into carbonic oxide and oxygen, in the reduction of the metallic oxides and in a great number of other reactions, brought about by heat. We will now place sulphur and carbon, whether free or combined, together.

4. *Sulphurous acid gas and carbon* (baker's embers calcined

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beforehand for several hours at a white heat, in a current of dry chlorine, then cooled in a current of nitrogen). Operating in a porcelain tube at a clear red heat, a gas was collected, formed of carbonic oxide, carbon oxysulphide, and disulphide in the following proportions :—

$$4SO_2 + 9C = 6CO + 2COS + CS_2,$$

a small quantity of sulphur being sublimed at the same time. All this is intelligible, on the supposition that the carbon took the oxygen,

$$SO_2 + 2C = 2CO + S_2,$$

and that the gaseous sulphur, being set free, combined for its own part partly with the carbon and partly with the carbonic oxide.

In these experiments the carbon contained in the tube becomes covered with a sort of sooty coating, and undergoes a remarkable disaggregation, which divides it into small fragments, according to three rectangular planes; phenomena which appear to be due to the state of dissociation peculiar to disulphide, which is partly destroyed at the same temperatures at which it is formed according to former observations.[1]

5. *Carbonic acid and sulphur.* The experiment was carried out at two different temperatures.

1st. The sulphur is raised to the boiling point in a glass retort, and a slow current of dry carbonic gas is passed through it. This reaction has been given as producing carbon oxysulphide. This is not the case, as the author has assured himself by most careful tests. What may have occasioned the error are the traces of sulphuretted hydrogen, which even the best purified sulphur always liberates when heated.

In reality, sulphur in a state of ebullition is without action on dry carbonic gas.

2nd. If carbonic gas mingled with sulphur vapour be passed through a porcelain tube at a clear red heat, a reaction, very slight it is true, but unquestionable, may, on the contrary, be observed.

Thus the gas liberated contained, out of 100 volumes, 2·5 vols. of gases other than carbonic acid, viz.—

1 vol. COS; 1 vol. CO; 0·5 vol. SO_2.

These small quantities seem to be attributable not to the action proper of sulphur on carbonic acid, but to the previous dissociation of the latter into carbonic oxide and oxygen; a dissociation which, moreover, is but slight under these conditions, but which the presence of sulphur, which unites at one and the same time with the oxygen and carbonic oxide, tends to render manifest.

[1] "Annales de Chimie et de Physique," 4e série, tom. xviii. p. 169.

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6. *Carbonic acid and sulphurous acid gas.* The two gases were mixed in equal volumes, passed into a glass tube, which was then sealed. After two hours and a half of strong sparks the author observed—

Diminution of volume	19 vols.
SO_2	31 „
CO_2	30 „
CO	20 „

Each of the gases was decomposed for its own part. The oxygen resulting from the dissociation of the carbonic acid was condensed, uniting with the sulphurous acid under the form of sulphuric acid.

The sulphurous acid gas here seems more stable than the carbonic acid gas, contrary to what might have been expected.

7. *Sulphurous acid gas and carbonic oxide.* 1st. The mixture made in equal volumes was slowly passed through a very small porcelain tube at a clear red heat. There was collected—

	Intermediate gas.	Final gas.
SO_2	47 vols. ...	37 vols.
CO_2	9 „ ...	20 „
CO	44 „ ...	43 „

Sulphur was formed. Neither carbon oxysulphide nor carbon disulphide was present in any considerable proportion.

Thus the carbonic oxide reduced the sulphurous acid gas—

$$2CO + SO_2 = 2CO_2 + S.$$

But the reduction remained incomplete, as the experiment made with carbonic acid permitted of foreseeing.

2nd. Two vols. of carbonic oxide and one vol. of sulphurous acid gas were mixed and passed into a glass tube provided with platinum electrodes, the tube being then closed. A series of sparks was passed through it. The following are the results of both trials :—

	After half an hour.	After two hours.
Diminution	14 vols. ...	28 vols.
SO_2	20 „ ...	6 „
CO_2	18 „ ...	9 „
CO	48 „ ...	57 „

No sulphur nor carbon oxysulphide. Here again we see the reduction of the sulphurous acid by the carbonic oxide. But, and it is a remarkable circumstance, a considerable portion of the former gas is destroyed for its own part without yielding its oxygen to the carbonic oxide, and giving the same compound of sulphur, sulphurous acid, and sulphuric acid already described, and which condenses on the walls of the tube.

3rd. The same experiment, repeated over mercury, with strong sparks, in the space of four hours caused the total

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destruction of the sulphurous acid gas, producing a final mixture containing—

CO_2	...	...	...	...	...	24 vols.
CO	...	...	...	...	...	75 „
O	...	...	...	...	...	1 „

Under these conditions the mercury absorbs the anhydrous sulphuric acid, and eliminates it, forming a sub-sulphate.

8. *Saline compounds.* All the alkaline oxysalts of sulphur being reduced to the state of sulphate and sulphide towards a red heat, special attention was paid to these two salts, together with potassium carbonate, and they were allowed to act at a red heat on sulphur, carbon, and their gaseous oxides. The salts were contained in elongated vessels arranged in a porcelain tube.

9. *Potassium sulphate and carbonic acid.* At a bright red heat, no action took place. At a higher temperature it would doubtless be important to take into account the dissociation of the sulphates observed by Boussingault.

10. *Potassium sulphate and carbonic oxide.* At a bright red heat the sulphate was charged into sulphide, or rather into polysulphide,[1] containing some flakes of carbon, and a mixture of carbonic acid and carbonic oxide was collected, the relative proportion of the former gas varying between four-fifths and the half, according to the speed of the current and the temperature.

The principal reaction here is—

$$SO_4K_2 + 4CO = K_2S + 4CO_2.$$

There is a trace of carbonate.

11. The reducing action of carbon on potassium sulphate is so well known that it was not deemed necessary to reproduce it.

12. *Potassium sulphate and sulphurous acid.* There is no action at a bright red heat.

13. *Potassium sulphate and sulphur.* Sulphur may be evaporated in presence of potassium sulphate, provided the temperature be carefully kept below a red heat.

On the contrary, in a red-hot porcelain tube, sulphur vapour reduces potassium sulphate, producing polysulphide and sulphurous gas—

$$SO_4K_2 + 4S = K_2S_3 + 2SO_2.$$

This transformation was never total. It seems, moreover, to represent the last term of a series of changes, in which the lower

[1] The constant formation of polysulphide in the actions caused by heat which yield sulphur, has been remarked by Gay-Lussac, Berzilius, and Bauer. It is connected with some imperfectly known reaction, such as the formation of an oxysulphide of potassium.

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oxysalts of sulphur intervene; compounds of which, in fact, traces may be found by moderating the action.

The well-known reaction of carbon disulphide on potassium sulphate, which it changes into sulphide, may be roughly regarded as the sum of those of sulphur and carbon. But according to Schöne it is also preceded by intermediate compounds, such as sulphocarbonate.

14. *Sulphur and potassium carbonate.* This is among the number of reactions which have received the greatest amount of investigation. At a red heat it yields polysulphide, sulphate, and carbonic acid—

$$4CO_3K_2 + 16S = 3K_2S_5 + SO_4K_2 + 4CO_2.$$

But these are also the extreme terms of successive reactions, hyposulphite, for instance, forming at 250°, according to Mitscherlich.

15. *Carbon and potassium carbonate.* This reaction yields at a red heat carbonic oxide and potassium oxide, not without there being formed various secondary compounds, such as the acetylides. The dissociation of potassium carbonate also intervenes (Deville).

16. *Potassium carbonate and sulphurous acid.* If the gas passes rapidly, the red-hot salt changes into sulphate, with only a trace of sulphide. If the current is slow the sulphide increases.

17. *Carbonic acid and sulphite.* Sulphate, polysulphide, and a little carbonate are formed. Metasulphite (anhydrous bisulphite) gives the same products.

18. *Carbonic acid and potassium polysulphide.* In a red-hot tube some sulphur is sublimed, and the gas liberated contains about three per cent. of a mixture of carbonic oxide, sulphurous acid, and oxysulphide. It is the same reaction as that of sulphur on carbonic acid, which is attributable to the dissociation of the latter compound. A small quantity of alkaline carbonate appears also to result from this dissociation; the oxygen supplied by the latter concurring with the excess of carbonic acid to displace the sulphur.

19. From these facts there result several consequences connected with the study of the reactions produced during the explosion of powder.

For example, if potassium carbonate subsists in any considerable amount in presence of sulphur resulting from the dissociation of the simultaneously produced polysulphide, it is apparently because both salts do not form at the same spot of the substance in ignition. The same sulphur would also attack the potassium sulphate if both bodies were kept together at the same point. The carbonic oxide would also destroy the sulphate if it were formed at the same spot, or if it remained for some time in contact with the melted salts, etc.

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Hence we see how the more or less homogeneous character of the initial mixture, the greater or less duration of combustion, and the varying rapidity of cooling may cause the nature of the final products to vary within very wide limits. There will be occasion to return to these problems, which have a great importance in practice.

20. Hitherto we have examined the final products of reactions taking place at a red heat. In these reactions neither sulphite nor hyposulphite is found, because both these classes of salts are decomposed below this temperature.

§ 3. Decomposition of the Alkaline Sulphites by Heat.

1. We shall distinguish between the neutral sulphites and the metasulphites formerly called anhydrous bisulphites.

The neutral potassium sulphite may be decomposed into sulphate and sulphide, according to theory—

$$4SO_3K_2 = 3SO_4K_2 + K_2S.$$

2. A special study was made of this decomposition, which forms one of the most striking distinctions between normal sulphites and metasulphites.

It was found that the accurate analysis of the products verifies the above equation in the most precise manner, when dry sulphite is brought to a dull red heat in an atmosphere of nitrogen.[1] Several estimations by iodine, made with the requisite precautions, absorbed, for instance, 31·5 c.c., 32·5 c.c., 30·8 c.c. of the iodine solution; while the original salt took up 126 c.c. The quarter of the latter figure is just 31·5.

No sulphurous acid is liberated, contrary to an assertion made by Muspratt, which would require an inexplicable setting free of potash.

The decomposition of the sulphite does not commence at 450°, the salt remaining intact till towards a dull red heat, and even at that temperature needing a certain time to be completely transformed.

3. It is well known that two series of sulphites are distinguished: the neutral, and the acid sulphites, supposed to correspond to the composition of a dibasic acid; viz. SO_2K_2O, and SO_2KHO, salts which have been studied by Muspratt, Rammelsberg, and De Marignac.

These investigators have further discovered an anhydrous bisulphite: $(SO_2)_2K_2O$.

In following up his researches on the products of the explosion of powder, the author has been led to measure the heat of

[1] Only the sulphite contains, as is always the case, some small amount of a red polysulphide, a compound which is met with under all the conditions in which the monosulphide alone should be formed.

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formation of these various potassium sulphites, and has found, not without surprise, that the so-called anhydrous bisulphite, far from belonging to the same type as the other sulphites, constitutes in reality, by its chemical reactions and thermal properties, a distinct and characteristic type of a new saline series, viz. the *metasulphites*, as distinct from the sulphites properly so called, as the metaphosphates and pyrophosphates, for example, are from the normal phosphates.

Pure potassium metasulphite is obtained by saturating with sulphurous acid gas a concentrated solution of potassium carbonate, either warm or even cold, and by drying at 120° the salt which separates by crystallisation. The anhydrous salt already described under the name of *anhydrous bisulphite* by Muspratt and Marignac corresponds to the formula $S_2O_5K_2$.[1] This salt is distinguished by its heat of formation, its stability, its tendency to form hydrates, and even solutions distinct from those of the normal bisulphite, and, finally, by its decomposition by heat. In lieed, the normal bisulphite prepared in dilute solutions by the saturation of the neutral sulphite by sulphurous acid soon changes state in the liquid itself. It is dehydrated, and becomes metasulphite, liberating + 2·6 Cal., a fact which accounts for the preponderance of the metasulphite and its definite formation in solutions.

The dissolved potash, moreover, reduces the metasulphite to the state of neutral sulphite.

Without dwelling any further here upon the characteristics of the metasulphites, we shall describe the action which heat has upon this one as entering into the scope of the present work.

4. *Decomposition of metasulphite by heat.* The action of heat forms one of the most striking characteristics of potassium metasulphite. In fact, dry metasulphite does not lose sulphurous acid even at 150°.

However, if it be brought to a dull red heat, it liberates sulphurous acid, but without regenerating a corresponding amount of neutral sulphite, and even changing in a well-defined and entire manner into potassium sulphate and sublimed sulphur when the reaction is carefully carried out—

$$2S_2O_5K_2 = 2SO_4K_2 + SO_2 + S.$$

This equation has been verified by accurate measurements. These are characteristic. Sulphurous acid is actually liberated. The volume of this gas indicated by the above formula should be the *half* of that corresponding to the normal reaction of a bisulphite, such as

$$S_2O_5K_2 = SO_3K_2 + SO_2.$$

[1] "Comptes Rendus des séances de l'Académie des Sciences," tom. xcvi. p. 142, and especially p. 208.

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Further, the neutral sulphite should be decomposed in its turn into sulphate and sulphide.

Now, the author has ascertained, operating in a very confined space filled with dry nitrogen, with a progressive heating, and collecting the gases as they were formed, to prevent their further reactions on the remaining salts—

1st. That the volume of the sulphurous gas is exactly the half of the volume required by the second formula (normal bisulphite).

2nd. That the salt residuum consists of almost pure sulphate, only exercising an insignificant action on an iodine solution.

The transformation is perfectly definite when the metasulphite alone is heated. In a current of an inert gas, such as nitrogen, or even in a considerable space filled with this gas, metasulphite commences to be decomposed into sulphurous acid, which is carried off, and neutral sulphite, which afterwards yields a certain amount of sulphide. But these complications may be avoided by operating as has been described. These reactions characterise metasulphite most distinctly.

§ 4. Decomposition by Heat of the Alkaline Hyposulphites.

1. On the occasion of the discussion which was raised some years since on the composition of the products of explosion of powder, the author showed that potassium hyposulphite, shown by former analyses to the extent of 34 per cent., does not in reality pre-exist in any appreciable proportion among these products, but is introduced during the analytical manipulations. This demonstration is based on the fact that potassium hyposulphite is entirely destroyed near 500°, a temperature far lower than that of the explosion of powder. It was finally accepted, not without opposition at the outset, by Noble and Abel, after the experiments of Debus, who proved that the hyposulphite found in the analysis resulted from the use of cupric oxide to eliminate the alkaline polysulphides.

The author since proved the same with zinc oxide. This oxide, acting on potassium polysulphide, yields besides zinc sulphide some hyposulphite, sulphate, and hyposulphate, the relative proportion of sulphur contained in the three latter bodies being 11·18 and 8 in one experiment. The presence of the hyposulphite in particular had escaped notice previously; it is probable that this body is produced also with cupric oxide. It is even formed, though only in small quantities, when polysulphide is destroyed by zinc acetate.

2. These facts being ascertained, it seemed desirable to determine more accurately the temperatures of decomposition of the alkaline hyposulphites. The experiments were made

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with salts dried in a progressive manner, at first, in vacuo, then at 150°, conditions under which they undergo no alteration.

If, on the contrary, they are suddenly heated to 200°, decomposition begins under the influence of the water vapour supplied by the hydrates.

When they are further heated, it is necessary to operate in an atmosphere of pure and dry nitrogen, the least trace of oxygen causing an oxidation and sublimation of sulphur. The decomposition of the hyposulphites is shown by analysis by means of iodine, which should be reduced to the half, according to the theoretical formula—

$$4S_2O_3K_2 = 3SO_4K_2 + K_2S_5.$$

The first body takes I_2, the second body only I.

The operations were carried out in an alloy bath, the temperatures being given by an air thermometer. With standardised solutions containing a known weight of iodine, the following results were obtained:—

	Amount of standard iodine used. Div.
$S_2O_3K_2$ according to theory	323
„ dried in vacuo	323
„ heated to 255°	325
„ 310° ten minutes	320
„ 310° an hour	323
„ 430° for a short time	320
„ 470°	160
„ 490°	161
$S_2O_3Na_2$ theoretical (another standardised solution)	632
„ dried at 150°	632
„ „ 200°	634
„ „ 255°	634
„ „ 331° ten minutes	633
„ „ 331° an hour	633
„ „ 358°	632
„ „ 400°	569
„ „ 470°	375
„ „ 490°	381

It results from these analyses that the potassium and sodium hyposulphites resist without alteration up to about 400°. The soda salt commences to alter at this temperature; the potash salt resists a little longer, up to about 430°, at least if the duration of the heating be not prolonged too much, otherwise it commences to change. At 470° the decomposition is total. It is strictly theoretical in the case of the potash salt. In that of the soda salt there occurs partial sublimation of sulphur, and the strength found is too high by about 8 per cent. (on 50).

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§ 5. On the Charcoals employed in the Manufacture of Powder.

1. In equations relative to the combustion of powder, pure carbon is usually considered; but in reality the charcoal should be taken with its true composition, for the results calculated on the supposition that the oxygen is in the state of water whilst carbon and hydrogen would be free, are not certain, owing to the complex composition of charcoal and the thermal excess which it liberates in its total combustion.

2. It might be imagined that, in order to take this fact into account in calorimetric calculations, it would be sufficient to calculate the formation of carbonic acid and carbonic oxide from amorphous carbon—

$$C + O_2 = CO_2 \text{ liberates } + 48{\cdot}5 \text{ Cal.},$$

instead of + 47 Cal. for diamond carbon.

But even this way of reckoning gives figures which are too low, because the charcoal used in the manufacture of powder is not pure carbon, but contains hydrogen and oxygen nearly in the proportions of water. For instance, the charcoal of the powder studied by Bunsen contained in 11·0 parts—

$$C = 7{\cdot}6;\ H = 0{\cdot}4;\ O = 3{\cdot}0.$$

Now, the combustion of the hydrocarbons yields more heat than that corresponding to the carbon they contain, the hydrogen and oxygen being supposed in the state of pre-existing water, that is to say, no longer contributing to the production of heat. Thus Favre and Silbermann,[1] burning bakers' embers (which contained to 1 grm. of carbon 0·027 grm. of hydrogen), found 52,440 cal., instead of 47,000 for 6 grms. of carbon burnt, which makes an excess of more than a ninth, or 906 cal. per gramme.

3. This is intelligible if it be noted that calcined charcoal is derived from a carbohydrate, and that the carbohydrates, as the author pointed out many years ago, yield by their combustion more heat than the carbon which they contain, deduction being made of the oxygen and hydrogen in the form of water.

The heat of combustion of a carbohydrate of the formula $(C_6H_pO_p)$ is, according to experiment, generally 709 Cal. to 726 Cal. for 72 grms. of carbon.

This would make for the heat of combustion of C = 6 grms. 59 Cal. to 61·6 Cal., that is, an excess of more than a fourth of the heat of combustion of the real carbon of the substance. When the carbohydrates are dehydrated by heat, a portion of

[1] "Annales de Chimie et de Physique," 3e série, tom. xxxiv. p. 420. 1852.

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this thermal excess, that is, a portion of this excess of energy, remains in the residual carbon.[1]

Further this latter carbon sometimes retains an excess of hydrogen which yields, weight for weight, four times as much heat as carbon.

4. It is hardly possible accurately to estimate the influence of these complex circumstances, unless by very special analysis and calorimetric determinations made on the charcoal employed in the manufacture of a given powder. But it is clear that they tend to reduce the error committed by assuming in the calorimetric calculations the weight of the charcoal employed as equal to the weight of pure carbon, than which it is really lower by about a fifth. This compensation extends itself even to the volume of the gases; since the deficiency in volume of carbonic acid produced is almost entirely replaced at the moment of the explosion by the volume of water vapour, resulting from the hydrogen and oxygen contained in charcoal.

5. With a view to rendering these notions clearer, we shall give some observations made on the composition of a charcoal derived from pure lignite. Having had occasion to see, in the powder factory at Toulouse, some spindle-tree charcoal, prepared with the ordinary precautions, that is to say protected from the air and at a relatively low temperature, from young branches containing a considerable quantity of pith, it was deemed of interest to examine the carbonaceous portion derived from this pith, a pure and homogeneous substance.

Further, the central position allows of the decomposition of the substance by heat taking place outside the influence of the the air and the gases formed by secondary reaction in the distilling apparatus. Some of the carbonised branches were obtained, and the charcoal contained in the medullary channel extracted and examined.

It retained exactly the appearance and structure of the original pith, except, of course, its colour. In order to analyse it, it was dried in an oven, and burnt in a current of oxygen, completing the combustion of the gases by a column of cupric oxide. Results:

(1) Loss at 100° ... ... 9·0

This loss is due to water, which can be absorbed by sulphuric acid. However, there is also produced a trace of carbonic acid, as was proved, which is doubtless produced by oxidation on contact with the air, which is worthy of notice, from the low temperature of the experiment (100°). But the weight is less than the one-thousandth part, from direct measurements.

(2) Ash ... ... 3·5

[1] See also the works of M. Scheurer-Kestner, who has found an analogous excess in the combustion of certain kinds of coal.

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(3) The combustible substance, dried at 100°, contained—

Carbon 73·6, that is, including the saline carbon of the ash	73·9
Hydrogen	2·2
Potassium	2·1
Oxygen	21·8

These numbers may be represented by the following empirical proportions, $C_{120}H_{43}KO_{27}$, which require—

C	73·7
H	2·2
K	2·0
O	22·1

Of course it will be understood that it is not the question here of a formula properly so called.

These proportions, compared with those expressing the composition of cellulose, $C_{120}H_{200}O_{100}$, show that distillation deprives this substance not only of an excess of water, but also of an excess of hydrogen, which corresponds with the formation of methane, CH_4, acetone, C_3H_6O, and analogous products. The charcoal of the pith is therefore not a simple carbohydrate, but contains a proportion of oxygen higher than that which would correspond to such a composition.

The proportion of oxygen contained in this charcoal, viz. 22 per cent., is very remarkable, on account of the physical properties of the substance. We are here in presence of special compounds having a very high equivalent, but the insolubility and amorphous state of which prevent their being properly determined. The author has elsewhere maintained the existence of these moist and carbonaceous compounds formed by successive condensations, and of which the various carbons represent the extreme limit.[1]

§ 6. Total Combustion Powders: Saltpetre and Charcoal.

1. Two combustible elements being associated with the combustive, it is easy to imagine an unlimited number of powders of this kind. We shall consider the three following cases:—

(1) Mixture of saltpetre and charcoal.

(2) Mixture of saltpetre and sulphur.

(3) Mixture of saltpetre with sulphur and charcoal in equal proportions.

[1] "Traité de Chimique organique," p. 384 (1872); 2e édition, tom. i. p. 456 (1881); "Annales de Chimie et de Physique," 4e série, tom. xix. p. 143, and tom. ix. p. 475. The analogy (tom. ix. p. 478) of these compounds with the metallic oxides obtained by a more or less intense calcination, and which represent products of successive condensation, was also maintained.

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(1) *Saltpetre and charcoal.* The equation is the following—

$$4KNO_3 + 5C = 2K_2CO_3 + 3CO_2 + 4N.$$

It corresponds to 101 grms. of nitre and 15 grms. of carbon; in all, 116 grms.; or, for 1 kgm., 129 grms. of charcoal and 871 grms. of nitre.

1. This being admitted, the heat liberated will be, for 1 equiv. of potassium nitrate employed to burn carbon, at constant pressure + 90·7 Cal., or + 91·2 Cal. at constant volume; or, for 1 kgm., 782 Cal. at constant pressure, or 786 Cal. at constant volume.

2. The reduced volume of the gases = 27·9 litres; or, for 1 kgm., 240·5 litres.

3. Permanent pressure $= \frac{240{\cdot}5 \text{ atm.}}{n - 0{\cdot}27}$, with the usual reservation relative to the liquefaction of carbonic acid.

(2) *Saltpetre and sulphur.* The equation is the following:—

$$2KNO_3 + S_2 = K_2SO_4 + SO_2 + 2N.$$

It corresponds to 101 grms. of nitre and 32 grms. of sulphur; in all, 133 grms.; or, for 1 kgm., 241 grms. of sulphur and 759 grms. of nitre. The sulphur may be considered as pure, in practice.

1. The heat liberated will be, for one equivalent, 87·0 Cal. at constant pressure, 87·5 Cal. at constant volume; or, for 1 kgm., 654 Cal. at constant pressure, 658 Cal. at constant volume.

2. Reduced volume of the gases = 22·3 litres for the equivalent; or 168 litres for 1 kgm.

3. The permanent pressure $= \frac{168 \text{ atm.}}{n - 0{\cdot}25}$, with the reservation of the liquefaction limit of sulphurous acid.

4. Theoretical temperature at constant volume, 3870°.

5. Theoretical pressure $= \frac{2545 \text{ atm.}}{n - 0{\cdot}25}$.

Note that under the conditions attending the use of black powder the sulphurous acid shown by the above equations does not appear.

(3) *Saltpetre, sulphur, and carbon, the latter in equal weights (black powder with excess of nitre.)* The equation of the reaction is—

$$10KNO_3 + 3S + 8C = 3K_2SO_4 + 2K_2CO_3 + 6CO_2.^1$$

It corresponds to 505 grms. of nitre, 48 grms. of sulphur and

[1] Admitting the following specific molecular heats:—CO_2 = 3·6; N = 2·4; CO_3K_2 = 151·0; SO_4K_2 = 16·6; SO_2 = 3·6 (see p. 141).

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48 grms. of carbon; in all, 601 grms.; or, for 1 kgm., 840 grms. of nitre, 80 of sulphur, and 80 of charcoal.

1. The heat liberated will be for the equivalent weight, 479·6 Cal. at constant pressure, or 481·2 Cal. at constant volume; or, for 1 kgm., 798 Cal. at constant pressure, and 801 Cal. at constant volume.

2. Reduced volume of the gases = 66·9 litres for the equivalent weight; or 111·3 litres for 1 kgm.

3. The permanent pressure $= \frac{111 \text{ atm.}}{n - 0{\cdot}27}$, with the reservation of the limit of liquefaction of carbonic acid.

4. Theoretical temperature, 4746°.

5. Theoretical pressure $= \frac{2046 \text{ atm.}}{n - 0{\cdot}27}$.

6. The heat produced slightly exceeds that of sporting and service powder. But the volume of the permanent gases developed by the latter is double that corresponding to a complete combustion. Hence the pressure is far lower for powder with excess of nitre than for sporting and service powders.

The complete combustion effected by an excess of nitre is therefore not advantageous from the point of view of the effects developed by the pressure of powder. This inferiority of powder with an excess of nitrate had already been discovered in practice.

7. However, it is worthy of remark that the compounds which are formed by the complete combustion of a powder with an excess of nitre, viz. potassium sulphate and carbonate, are also noticed by writers on the subject as principal products in the deflagration of sporting and service powder, as well as in that of powders the most different in appearance, such as blasting powder, which is very rich in sulphur, and powder with an excess of charcoal. Although the products vary a little with the conditions of deflagration, potassium sulphate and carbonate have almost always been observed, and this is the more important, as these two salts do not figure in the theoretical equations formerly admitted.

§ 7. Service Powders.

1. We shall divide the study of service powders into four sections, comprising—

(1) The general properties of powder.
(2) The products of combustion of powder.
(3) The theory of combustion of powder.
(4) The comparison between theory and observation.

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(1) *General Properties of Powder.*

1. The proportion, "*six, ace* and *ace*," that is to say—

Saltpetre	75·0
Sulphur	12·5
Charcoal	12·5

has never been far departed from in France. An excess of charcoal and of nitre increases the strength; an excess of sulphur has been found favourable to the preservation of powder. The presence of sulphur, moreover, lowers the initial temperature of the decomposition of the substance and regulates it. The actual proportions in France are—

	Nitre.	Sulphur.	Charcoal.
Ordnance powder	75	12·5	12·5
Old coarse grained powder	75	10	15
Rifle powder, Class B	74	10·5	15·5
Rifle powder, Class F	77	8	15
Austria	75·5	10	14·5
United States, Switzerland	76	10	14
Holland	70	14	16
China	61·5	15·5	23
Prussia	74	10	16
England, Russia, Sweden, Italy	75	10	15

The composition 75, 12·5, 13·5, corresponds practically to the relations

$$2KNO_3 + S + 3C,$$

or 101 + 16 + 18; in all, 135 grms.; or, for 1 kgm., 748 grms. of saltpetre, 118·5 grms. of sulphur, and 133·5 grms. of carbon.

2. The temperature of inflammation of powder was fixed at 316° by Horsley. This temperature varies with the process of heating. It may fall to 265°, according to Violette.

If the heating takes place slowly, the sulphur melts, causes the aggregation of the grains, then gradually vaporises and may even be almost entirely sublimed. The nature of the charcoal has great influence in this case; some wood charcoals yielding carbonic acid on contact with the air at 100° and even below p. (489).

It is, therefore, natural to suppose that such charcoals, if their surface be not completely covered by sulphur and saltpetre through a very intimate mixture, may become more and more rapidly oxidised at a temperature which moreover goes on increasing owing to the oxidation. They may even take fire, especially if the mass be so large that the heat produced by this oxidation has not time to dissipate itself. We may in this way account for certain accidents caused by spontaneous inflammation of heaps of powder dust.

3. The inflammation of powder is caused by the shock of iron on iron, iron on brass or marble, brass on brass, quartz on quartz, less easily by iron on copper, or copper on copper. It

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is caused even by lead on lead, or lead on wood; seldom by copper on wood, never by wood on wood, without of course the interposition of gravel.

4. Powder absorbs a certain amount of moisture, principally owing to the hygroscopic properties of the charcoal and the impurities of the saltpetre; this amount varying from 0·5 in dry magazines to 1·20 in damp magazines. The proportion of water thus absorbed may rise to seven per cent. in a saturated atmosphere, the temperature of which undergoes alternate changes. When it exceeds a certain limit it causes the separation of the saltpetre by eventual efflorescence, thus destroying the powder.

5. The density of powder has been considered from three points of view:

1st. *The absolute density*, defined in the sense in which it is employed by physicists.

2nd. The apparent density of the isolated grains, called *real density*.

3rd. The apparent density of unrammed powder, called *gravimetric density* (weight of powder at the unit of volume). The gravimetric density varies from 0·83 to 0·94, according to the coarseness of the grain.

The so-called real density is found by plunging a given weight of powder into a given medium of which the variation of volume is observed. The following substances have been used:—lycopodium, a solid body in a very fine powder, essence of turpentine, water saturated with saltpetre, absolute alcohol, and mercury; the latter being the only liquid which can be considered as exercising no dissolving action.

In the tests, it is subjected to a fixed pressure (2 atm.) during the operation. The results obtained in this way have only a relative significance.

The following have been found in this manner:—

Ordnance powder	1·56 to 1·72
Rifle powders	1·63 to 1·82
Sporting powder	1·87

The absolute density, measured by the volumometer, is 2·50.

(2) *Products of Combustion of Powder.*

1. These products are those of the combustion of charcoal and sulphur by oxygen, modified by the presence of nitrogen and the reaction between these products and potassium, proceeding from the saltpetre, at the high temperature of combustion.

2. The proportions of the composition of powder are not those of total combustion, oxygen being wanting; they therefore do not correspond to the greatest heat which might be liberated by the oxidation of the sulphur and carbon by a given weight

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of saltpetre. On the other hand, they yield a much greater volume of gas, which compensates, so that the strength of such a powder is after all superior to that of a total combustion powder. It will be seen that this fact must introduce some complication into the chemical reactions.

3. The latter, moreover, change greatly in character with the pressure, when operating in a closed vessel. They are also modified during the discharge of firearms owing to the rapid expansion of the gases. But the analytical experiments then become very delicate owing to the difficulty of collecting the products, and preventing them from undergoing at this moment the oxidising action of the air, which is the more to be apprehended, the more divided the pulverulent products are.

4. Let us now go into detail. Observation shows that the combustion of powder produces as principal products the following bodies (neglecting certain accessory substances to which we shall return later on):—

Potassium carbonate, sulphate, and sulphide, or rather, polysulphide, carbonic oxide, and nitrogen.

There subsists no sulphurous acid, nor carbon, nor oxygenated compounds of nitrogen, whether free or in the saline form (except sometimes some nitrite).

5. These results are accounted for in the following way. At first the salts of the lower oxygenated acids of sulphur and nitrogen are all decomposed by the high temperature of the explosion. As for sulphurous and hyponitric acids, they are reduced by the carbon and carbonic oxide (see p. 480).

6. Nevertheless, some traces of accessory products are obtained, such as water, ammonium carbonate, potassium hyposulphite, and sulphocyanide, sulphuretted hydrogen, hydrogen and methane; all these bodies being due to secondary reactions, or reactions developed during cooling. We shall presently return to them.

7. We have now to examine the relative proportions of the various products. We shall first define the initial state.

8. *Initial state.* The analyses were made on powders, the composition of which was nearly the following:—

Saltpetre	74·7
Sulphur	10·1
Charcoal	14·2[1]
Water	1·0

These numbers, taken roughly, approach the following relations:

$$16KNO_3 + 21C + 7S,$$

in the vicinity of which the composition of the powder of the

[1] The charcoal used contained in 14·2 parts: pure carbon, 12·1; hydrogen, 0·4; oxygen, 1·45; ashes, 0·2.

Nitre	772·5
Carbon	120·5
Sulphur	107

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principal nations would fluctuate, according to Debus. These relations expressed in weights represent; 1616 grms. of nitre, 252 grms. of carbon, 224 grms. of sulphur; in all, 2092 grms., which makes per kilogramme 772·5 grms. nitre, 120·5 carbon, 107 sulphur.

It should be observed that in this estimate three to four per cent. of matter are neglected, represented by moisture (1·0), ash (0·2 to 0·3), and especially by the hydrogen (0·4 to 0·5) and oxygen (1·5 to 2·5) of the charcoal. The moisture and ash have little influence; but the hydrogen and oxygen of the charcoal modify sensibly the volume of the gases. They increase above all the heat liberated, to such a degree, that the difference between the latter calculated from the weight of carbon supposed pure and the real heat amounts at least to a tenth, and with some kinds of charcoal might even rise to the fourth of the former quantity (see p. 488).

9. *Final state.* We are indebted to Noble and Abel for a long and important work on this question. They effected the combustion of powder in a closed vessel; a condition which is not quite the same as that of the combustion of powder in fire-arms, on account of expansion, and also of the action on the walls of the vessels, with the formation of iron sulphide, a compound which was produced in very considerable quantities in their experiments. The mean density of the products of combustion varied in their experiments from 0·10 to 0·90. The following are the proportions by weight of the products observed:—

	Pebble Powder, W.A.		R.L.G. Powder, W.A.		F.G. Powder, W.A.	
		Mean.		Mean.		Mean.
CO_2 . . .	25·0 —27·8	26·8	24·8 —27·6	26·3	24·9 —28·9	26·9
CO . . .	5·7 — 3·7	4·8	5·8 — 3·1	4·2	5·8 — 2·6	3·5
N	11·0 —11·2	11·5	12·3 —10·5	11·2	11·7 —10·6	11·2
H	... ...	0·06	0·4 — 0·03	0·1	0·1 ...	0·07
H_2S . . .	1·8 — 0·7	1·1	1·8 — 0·8	1·1	1·5 — 1·0	0·8
CH_4 . . .	1·14— 0·0	0·06	0·17— 0·01	0·08	0·1 ...	0·04
O	0 ...	0	0·2 ...	...	0·1 — 0	0·03
Total gaseous products .	43·2 —44·8	44·1	42·1 —43·7	43·0	41·5 —43·7	42·8
K_2CO_3 . .	37·1 —29·8	37·1	38·0 —28·8	34·1	34·3 —25·1	28·6
K_2SO_4 . .	5·3 — 8·6	7·1	2·8 —14·0	8·4	10·4 —14·0	12·5
K_2S . . .	12·5 — 6·7	10·4	10·9 — 6·2	8·1	12·1 — 4·7	10·0
S	6·2 — 2·3	4·4	7·2 — 2·7	4·9	5·8 — 2·3	3·8
KCyS. . .	0·3 — 0·003	0·14	0·2 ...	0·1	0·15 ...	0·07
$(NH_4)_4(CO_2)_3$	0·09— 0·03	0·05	0·08— 0·02	0·04	0·09— 0·01	0·09
Charcoal . .	... ...	0·08	0·4 ...	0·04	... ...	...
KNO_3 . .	0·27— 0·0	0·13	0·33 ...	0·15	0·16— 0·05	0·09
K_2O . . .	... ...	...	... ...	3·1	... ...	0·6
Total solid products .	55·9—54·2	55·0	56·7 —55·2	55·9	57·0 —54·8	55·7
Water . .	... ...	0·95	1·1 ...	...	1·5 ...	...

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The variations are wider when we pass to powders in which the proportion of nitre is different, such as sporting and blasting powders, but we suppress these data in order not to unduly extend our explanations.

10. These analyses give rise to various remarks. It should in the first place be noted that the sulphur observed is not free in reality, but combined, partly in the form of potassium polysulphide, and partly as iron sulphide (or rather of double sulphide of iron and potassium), resulting from the action on the walls of the vessels. This phenomenon manifested itself to the greatest extent in Noble and Abel's experiments, but it is far less appreciable in firearms owing to the rapidity with which the products are cooled by expansion and expelled.

11. For a long time potassium hyposulphite, which appears in the analyses of Bunsen, Linck, Federow, and in the early publications of Noble and Abel, as representing an amount sometimes very considerable, had been admitted among the products of the combustion of powder. The author had called attention some years since to the fact that this compound could not be an initial product of the combustion of powder, since it is completely decomposed by heat towards 450° into sulphate and polysulphide (see p. 487). At the very most the presence of some trace of it might be admitted, due to the secondary reactions taking place during cooling. But the considerable amounts observed by writers on the subject appeared attributable to the alteration of the products produced both by contact with the air and during the analytical manipulations.

Shortly afterwards Debus confirmed this opinion, and discovered that the hyposulphite found was attributable chiefly to the reactions of the potassium polysulphides on the copper oxide employed in the analysis to separate the sulphur from the alkaline sulphide. Thus at the present day hyposulphite has disappeared from the list of the essential products formed during the combustion of powder.

12. It will further be remarked that in exceptional cases a small quantity of charcoal escapes combustion. A small quantity of nitre up to three thousandth parts is almost always found.

Lastly, some powders would yield free potash up to three per cent.; a sign of some dissociation of which the suddenness of cooling or of solidification has preserved a trace; this potash not having had time to unite with the carbonic acid of the superposed atmosphere.

The free oxygen which would result from some analyses may be attributed either to particles of nitrate remaining isolated in the mass and decomposed by the high temperature of the explosion, or more probably to the dissociation of the carbonic acid (see p. 504), and the sudden cooling of the mass, which did not

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allow this oxygen to recombine with the excess of carbon or sulphur.

13. Hydrogen and methane are unimportant products, due to the complex composition of the charcoal.

The sulphocyanide appears to result from the action of the sulphur on a small quantity of potassium cyanide, which may be formed, as is well known, in the reaction of carbon in excess on potassium nitrate.

A portion of this cyanide changed into cyanate by the oxidising action, then decomposed by water vapour during cooling, appears to be the origin of the ammonium carbonate.

The same reaction of water vapour and the co-existing carbonic acid on the alkaline sulphide explains the formation of a small quantity of sulphuretted hydrogen.

14. *Equivalent relations.* If, for the sake of simplicity, the accessory products (sulphuretted hydrogen, methane, hydrogen, sulphocyanide, oxygen, ammonium carbonate, etc.) be neglected, we find the following equivalent relation between the principal products :—

POWDER.

	Pebble.		R.L.G., W.A.		F.G., W.A.	
	mean.	deviation.	mean.	deviation.	mean.	deviation.
CO_2	1·22	0·08	1·20	0·06	1·22	0·09
CO	0·84	0·023	0·30	0·07	0·25	0·19
N	0·80	0·05	0·80	0·08	0·80	0·05
K_2CO_3	0·54	0·11	0·50	0·08	0·41	0·11
K_2SO_4	0·08	0·02	0·10	0·06	0·14	0·02
K_2S	0·19	0·07	0·15	0·05	0·19	0·10
S	0·28	0·13	0·30	0·14	0·24	0·12

The general mean of the analyses would not differ greatly from the following relation proposed by Debus :—

$$16KNO_3 + 21C + 7S = 13CO_2 + 3CO + 5K_2CO_3 + K_2SO_4 + 2K_2S_3 + 16N.$$

15. *Variations in the composition of the final products.* But this mean does not take into account the variations amounting in the case of carbonic oxide to from 2·6 to 5·8; in that of potassium carbonate from 25·1 to 38·0; the sulphate from 2·8 to 14·0; the sulphide from 4·7 to 12·5.

Generally speaking, the amount of carbonic acid and potassium carbonate increases slightly (except F.G., W.A. for the latter) with the pressure; while the carbonic oxide tends to diminish (except F.G., W.A.).

The potassium sulphate, sulphide, and carbonate must contain the whole of the potassium. Hence no one of these three salts can vary without the whole of both the others undergoing a

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complementary change. Similarly the carbon will be shared between the potassium carbonate, carbonic acid, and carbonic oxide, which are complementary. The variations in the sulphur have less influence on the other compounds, owing to the formation of the polysulphide, which absorbs a variable excess of this element. The nitrogen becoming free almost in its entirety does not enter into account.

The free carbonic acid changes but little.

But the variations in the carbonic oxide and carbonic acid, combined with the potassium, are complementary to the more or less advanced transformation of the sulphate into sulphide.

We are about to attempt to account, by a theory, for the formation of the fundamental products, together with the fluctuations observed in their relative proportions.

3. *Theory of the Combustion of Powder. Simultaneous Equations.*

1. In the case of powder, as well as in that of ammonium nitrate (p. 5), and generally of the substances which do not undergo total combustion, several simultaneous reactions are produced, due to the diversity of the local conditions of combustion in the unavoidable absence of homogeneousness in a purely mechanical mixture of three pulverised bodies, and to the rapidity of the cooling of the mass, which does not allow of the reactions attaining their limits of definite equilibrium. If we limit ourselves to the principal products these equations may be reduced to the following:—

(1) $2KNO_3 + S + 3C = K_2S + 3CO_2 + 2N$
(2) $4KNO_3 + 5C = 2K_2CO_3 + 3CO_2 + 4N$
(3) $2KNO_3 + 3C = K_2CO_3 + CO_2 + CO + 2N$
(4) $2KNO_3 + S + 2C = K_2SO_4 + 2CO + 2N$
(5) $2KNO_3 + S + C = K_2SO_4 + CO_2 + 2N$

By combining them with each other, two by two, three by three, etc., we obtain systems of simultaneous equations representing all the analyses, the extreme as well as the intermediate cases.

In this way equations less numerous, but more complicated, are formed, which any one may combine so as to represent any particular circumstance of the explosion to which he attaches a special importance. But all these arrangements essentially belong to an analogous conception. Representations of this kind are, moreover, indispensable, unless by an arbitrary fiction we suppress the experimental variations, which it is precisely the object of the simultaneous equations to express.

2. On the contrary, by devoting exclusive attention to the variations, one would run the risk of falling into a blind

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empiricism, incapable of serving as guide for the perfecting of the practical applications. We shall now apply these ideas in detail. Take, for instance, the mean value given above, according to Debus (p. 498); it corresponds to an equation which is too complicated to be admitted as the general representation of the phenomenon, but it is easy to see that it results from a certain system of transformations in which a fourth of the saltpetre has been destroyed according to equation (1)—the sulphide, moreover, having been changed into polysulphide at the expense of the excess of sulphur; an eighth of the saltpetre has been destroyed according to equation (5); three-eighths according to equation (3); and a fourth according to equation (2).

On the other hand, the analyses which have given the maximum of carbonate also correspond to the maximum of carbonic oxide, and to a very small proportion of sulphate, all these being correlative circumstances which may be expressed by the system according to simultaneous equations, viz. equation (1) for a third of the saltpetre; equation (3) for the half; equation (2) for about a sixth.

The opposite extreme is that in which the potassium sulphate gives the maximum proportion, or a fifth of the potassium; while the carbonate retains the half of it, and the carbonic oxide tends to disappear. These relations still show regular reactions, always expressed by a certain system of simultaneous equations: or equation (1) for a third of the saltpetre, and equation (2) for nearly the half, which corresponds to the carbonate; while the formation of potassium sulphate would correspond for an eighth of the substance to equation (4), and for a twelfth to equation (5).

3. The five simultaneous equations, therefore, represent the extreme cases; but it is easy to prove that their combinations also represent in an approximate manner the intermediate cases.

Consequently, the system of equations expresses the chemical transformation of powder, at least as regards the fundamental products. Further, it represents the variations, which could not be done by a single equation.

The transformation reduces itself definitively to five simple reactions, which cause the formation of the potassium sulphate, sulphide, and carbonate, of carbonic acid, and carbonic oxide.

4. It is also easy to prove that the combustion of any powder may be represented by a certain combination of the above five equations; the first members being taken in such relative proportions that they represent the initial composition of the powder under consideration, provided the more or less abundant formation of the polysulphide, and of the deficit of about a fourth compared with real carbon, which results from the use of charcoal, be taken into account.

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5. The chemical transformation of powder being thus defined, let us now calculate the heat liberated and the volume of the gases produced, according to each of the five equations regarded separately.

6. Equation (1),

$$2KNO_3 + S + 3C = K_2S + 3CO_2 + 2N,$$

represents 135 grms. of matter; or, for 1 kgm., 784 grms. of nitre, 118·5 grms. of sulphur, 133·3 grms. of carbon. The products being, 408 grms. K_2S, 488 grms. CO_2, 104 grms. N.

The reaction liberates + 73·4 Cal. at constant pressure, 74·5 at constant volume, a quantity which the formation of the polysulphide, K_2S_5, by an excess of sulphur during cooling would raise to about 77 Cal.[1] This figure itself is calculated with the aid of data obtained at the ordinary temperature. At the high temperature of the explosion it is modified by various circumstances, such as the partial dissociation of the carbonic acid, the state of fusion, or even of volatilisation, of the potassium sulphide, the variation in the specific heats, etc. But it is not possible in the present state of the science to take these various circumstances into account; we shall therefore confine ourselves to the calculation based upon the data observed. These remarks apply likewise to the other equations.

Supposing, therefore, + 73·4 or 74·5 liberated by the transformation (1); this quantity, referred to 1 kgm., becomes 544 Cal. at constant pressure, or 552 Cal. at constant volume.

The reduced volume of the gases is 44·6 litres, or, for 1 kgm., 330·4 litres.

Permanent pressure $= \frac{330{\cdot}4 \text{ atm.}}{n - 0{\cdot}12}$, with the usual reservation of the liquefaction of carbonic acid for small values of n.

Theoretical temperature[2] = 3514°.

Theoretical pressure[3] $= \frac{4592 \text{ atm.}}{n - 0{\cdot}12}$, or $\frac{5740 \text{ atm.}}{n}$, assuming the total vaporisation of the potassium sulphide.

[1] It is here supposed that $C + O_2 = CO_2$ liberates + 47·0 Cal. See remarks on page 488.

[2] The following specific heats are taken—

CO_2	3·6	(at constant volume)
N	2·4	" "
CO	2·4	" "
K_2S	8.0	
CO_3K_2	15·0	
SO_4K_2	16·6	

They are supposed constant for the sake of simplicity.

[3] The real density of sulphide of potassium not being known, a density nearly equal to 3 has here been taken.

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7. These figures would be appreciably modified if we assumed, as was formerly done, the *total vaporisation of the saline compounds* at the moment of the explosion, which would increase the volume of the gases by a fourth, while slightly diminishing the heat liberated. But this hypothesis appears to be abandoned by nearly all specialists at the present day. It might, however, be true for potassium sulphide, a body which is volatilised at a red heat. It should further be observed that the theoretical temperature is too high, as in all calculations of this kind, owing to dissociation and the variation in the specific heats with the temperature. This tends to lower the theoretical pressure. But there is, as we have said elsewhere (p. 11), a certain compensation, due to the fact that in greatly compressed gases the variation of pressure with temperature is far smaller than would be indicated by Mariotte's and Gay-Lussac's laws. All these remarks apply equally to the other equations above set forth, and which we are about to discuss.

8. If the substance used contained a certain proportion of sulphur in excess and this sulphur were changed into iron sulphide (p. 497), 11·9 Cal. should be added per equivalent of iron sulphide. The heat liberated will therefore be increased. This increase represents one-eighth of the heat liberated; but the increase in the relative weight for an equivalent of sulphur is nearly the same, which forms a compensation for the same weight of matter.

These observations are equally applicable to the other equations.

9. Equation (2),

$$4KNO_3 + 5C = 2K_2CO_3 + 3CO_2 + 4N,$$

represents 116 grms. of matter, or, for 1 kgm., 129 grms. of carbon and 878 grms. of nitre. The products being, 593·6 grms. CO_3K_2, 284·5 grms. CO_2, 120·5 N.

The reaction liberates + 90·1 Cal. at constant pressure, or 90·8 Cal. at constant volume; or, for 1 kgm., 777 Cal. at constant pressure, or 783 Cal. at constant volume.

The reduced volume of the gases = 27·9 litres; or, for 1 kgm., 240·5 litres.

$$\text{Permanent pressure} = \frac{240{\cdot}5 \text{ atm.}}{n - 0{\cdot}27}, \text{ with the usual reservation.}$$

$$\text{Theoretical temperature} = 3982°.$$

$$\text{Theoretical pressure} = \frac{3749 \text{ atm.}}{n - 0{\cdot}27}.$$

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10. Equation (3),

$$2KNO_3 + 3C = K_2CO_3 + CO + CO_2 + 2N,$$

represents 119 grms. of matter; or, for 1 kgm., 106 grms. of carbon and 894 grms. of nitre. The products being, 580 grms. CO_3K_2, 117·5 grms. CO, 117·5 grms. N, 185 grms. CO_2.

The transformation liberates + 80·1 Cal. at constant pressure, + 80·9 Cal. at constant volume; or, for 1 kgm., 673 Cal. at constant pressure, 680 Cal. at constant volume.

The reduced volume of the gases = 33·5 litres; or, for 1 kgm., 281·5 litres.

Permanent pressure = $\frac{281{\cdot}5 \text{ atm.}}{n - 0{\cdot}26}$, with the usual reservation.

Theoretical temperature = 3458°.

Theoretical pressure = $\frac{3847 \text{ atm.}}{n - 0{\cdot}26}$.

11. Equation (4),

$$2KNO_3 + S + 2C = K_2SO_4 + 2CO + 2N,$$

represents 129 grms. of matter; or, for 1 kgm., 124 grms. of sulphur, 93 grms. of charcoal, and 783 grms. of nitre. The products being, 675 grms. SO_4K_2, 217 grms. CO, 108 grms. N.

The transformation liberates 78·2 Cal. at constant pressure, 79·0 Cal. at constant volume; or, for 1 kgm., 606 Cal. at constant pressure, 612 Cal. at constant volume.

The reduced volume of the gases = 33·5 litres; or, for 1 kgm., 260 litres.

Permanent pressure = $\frac{260 \text{ atm.}}{u - 0{\cdot}25}$, with the usual reservation.

Theoretical temperature = 3320°.

Theoretical pressure = $\frac{3422 \text{ atm.}}{n - 0{\cdot}25}$.

12. Equation (5),

$$2KNO_3 + S + C = K_2SO_4 + CO_2 + 2N,$$

represents 123 grms. of matter; or, for 1 kgm., 821 grms. of nitre, 130 of sulphur, 49 grms. of carbon. The products being, 708 grms. SO_4K_2, 178 grms. CO_2, 114 grms. N.

The transformation liberates + 99·4 Cal. at constant pressure, + 100 Cal. at constant volume.

The reduced volume of the gases = 22·3 Cal.; or, for 1 kgm., 181·5 litres.

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Permanent pressure $= \frac{181{\cdot}5 \text{ atm.}}{n - 0{\cdot}26}$, with the usual reservation.

Theoretical temperature = 4425°.

Theoretical pressure $= \frac{3122 \text{ atm.}}{n - 0{\cdot}26}$.

The five foregoing equations are the only ones which it is necessary to take into account in problems relating to service powder where the whole of the charcoal disappears, as has been said.

13. However, the study of blasting powder, which contains an excess of charcoal, has led us to consider a fresh reaction, that of charcoal on carbonic acid. This reaction appears due to the previous decomposition of the latter producing free oxygen capable of changing in its turn the carbon into oxide.

$$CO_2 = CO + O \text{ (partial dissociation) absorbs } - 34{\cdot}1;$$
$$C + O = CO \text{ (oxidation) liberates } + 12{\cdot}9.$$

It already plays a part in two of our equations, for it allows of passing from (3) to (2), and from (5) to (4).

Without dwelling on the intermediate cases, we shall consider the hypothesis of a decomposition as far advanced as possible, a hypothesis which never really applies to any but a portion of the substance.

Take, therefore, the equation

$$2KNO_3 + S + 6C = K_2S + 6CO + 2N.$$

It represents 153 grms.; or, for 1 kgm., 105 grms. of sulphur, 235 grms. of carbon, 660 grms. of nitre. The products being, 360 grms. K_2S and 640 grms. CO.

The heat liberated is 9·8 Cal. at constant pressure, or 11·4 at constant volume; or, for 1 kgm., 64 Cal. at constant pressure, or 74·5 Cal. at constant volume.

The reduced volume of the gases = 66·9 litres; or, for 1 kgm., 437 litres.

Permanent pressure $= \frac{437 \text{ atm.}}{n - 0{\cdot}11}$.

Theoretical temperature = 501°.

Theoretical pressure $= \frac{1304 \text{ atm.}}{n - 0{\cdot}11}$.

The heat liberated is very slight, and the theoretical temperature so low that this reaction can hardly be regarded as explosive.

14. If the foregoing results be compared from the point of

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view of the heat liberated and the volume of gases produced by a given weight of nitre, we obtain the following table—

	Equivalent weight.	Heat at constant volume.		Volume of the gases.		Theoretical pressures.
		1 equiv.	1 kgm.	1 equiv.	1 kgm.	
	grms.	Cal.		litres.		atm.
(1)	135	74·5	552	44·6	330	$\frac{4592}{n - 0·12}$
(2)	116	91·4	783	27·9	240·5	$\frac{3749}{n - 0·27}$
(3)	119	80·9	680	33·5	281·5	$\frac{3847}{n - 0·26}$
(4)	129	79·0	612	33·5	260	$\frac{3422}{n - 0·25}$
(5)	123	100·0	813	22·3	181·5	$\frac{3122}{n - 0·26}$
(6)	153	11·4	74·5	66·9	437	$\frac{1304}{n - 0·11}$

15. Equation (5) would be that liberating the maximum heat, if this maximum still subsisted at the temperature of combustion, in spite of the variation in the specific heats. Hence it seems that this reaction should take place to the exclusion of the others. In any case it should be so with the integral transformation of the oxygen by the carbon changed into carbonic acid in accordance with equations (2) and (5).

16. But these preponderating productions are checked by the following circumstances :—

(1) Dissociation, which does not allow either the whole of the potassium sulphate or the whole of the carbonic acid to be formed at the high temperature developed by the combustion.

(2) The change in the constitution of the sulphur at this high temperature (see p. 27), a change which tends to increase in an imperfectly known but certainly considerable proportion the heat of formation of the compounds of this element. This fact may play a specially important part in the way of increasing the thermal importance of the polysulphides.

(3) The change in the constitution of the carbon at a high temperature; this element existing in the gaseous state, at least for an instant, in the flames, and the heat of formation of carbonic oxide being then increased so as to become equal to, or perhaps higher than, that of carbonic acid for the same weight of oxygen.[1]

Owing to these circumstances the thermal maximum calcu-

[1] "Annales de Chimie et de Physique," 4e serie, tom. xviii. pp. 162 and 175, 176; 1869. "Revue Scientifique," Novembre, 1882, pp. 677–680.

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lated for the ordinary temperature may be very different from the thermal maximum near 2000° or 3000°, temperatures approaching that of the explosion of powder.

(4) The rapidity of cooling is too great for the products formed at the first instant to have time to react on one another so as to reconstitute the most stable system.

The specific rapidity of each reaction (p. 40) plays here a most important part, both at the moment of the initial formations which take place at the highest temperature, and during the successive reactions.

It should further be noted that cooling is more rapid at the point of contact with the walls of the vessels, when operating in a closed vessel, than towards the centre of the mass. Hence the composition is different at the various points of the mass, apart from the reactions exercised by the substances of the walls themselves, such as the formation of iron sulphide.

17. The rapidity of cooling is very different according as combustion takes place in a closed vessel strong enough not to be broken; or in a shell which bursts suddenly, the fragments being projected and a portion of the heat being transformed into mechanical work; or again in a firearm, where the expansion of the gases takes place according as the projectile is thrust forward and the gases themselves are continually expelled towards the cold portions of the metallic tube. The variation in the chemical reactions which may result from these different circumstances would be very interesting to study, but it has not been fully examined.

18. We shall, however, note that according to thermochemical principles the progressive reactions produced during cooling must be such as to liberate increasing quantities of heat.

In principle, when operating without changing the condensation of the substance—that is to say, at constant volume—it cannot be admitted, in the author's opinion, that endothermal reactions, such as dissociations, succeed during the period of cooling to a total combination produced at the instant of explosion. The dissociation must, generally speaking, be regarded as being at its maximum at the outset, that is, at the moment when the temperature is highest, and diminishing as cooling progresses. This applies principally to reactions effected in closed and resisting vessels.

It is only when expansion takes place at constant temperature, owing to the increase in the volume of the gases, that dissociation, regarded as a function of the pressure, could increase; the possibility of this increase may even be conceived, strictly speaking, in a case of this sort during a certain period of the cooling.

But these are quite exceptional cases, and endothermal

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reactions cannot in general be admitted during the period of rapid cooling succeeding combustion.

19. Let us now compare the volume of the gases liberated. The reactions of powder, according to the table on page 505, liberate a volume of gas greater in proportion as they develop less heat.

The minimum of gaseous volume (22·3 litres) corresponds to the thermal maximum (100·0 Cal.), and *vice versâ* (66·9 litres and 11·4 Cal.).

The gases may also vary from the single to the double, the heats only changing by a fifth, with the exception, however, of the transformation (6).

20. Hence follows this interesting consequence, that the theoretical pressure appears to be the greatest for the transformation liberating the least heat (except 6); it would, on the contrary, be the smallest for that liberating the most.

In fact, several transformations take place at the same time owing to local conditions of temperature, dissociation, and relative rapidity of combination. The heat liberated, the volume of gases, and therefore the pressure, will consequently remain intermediate between these extreme limits.

4. *Comparison between Theory and Observation.*

1. Such are the general consequences of the theory. We are about to show that observation confirms these consequences by summing up the results of the experiments, especially of those made by Noble and Abel, which have been carried out with greater care than any others.

2. Take first the mean equation (p. 498)—

$$16KNO_3 + 21C + 7S = 13CO_2 + 3CO + 5K_2CO_3 + K_2SO_4 + 2K_2S_3 + 16N.$$

Equation (1) × 2 + eq. (5) × 1 + eq. (3) × 3 + eq. (2) + 2.

Further, it is supposed that the excess of sulphur has been changed into trisulphide, K_2S_3.

According to this mean equation, 964 grms. of matter would have yielded 674·5 Cal. at constant volume, developing 290·1 litres; or, for 1 kgm., 697 Cal. and 300 litres.

The theoretical pressure would be $\frac{4350 \text{ atm.}}{n - 0{\cdot}26}$.

3. Take, now, the transformation observed which produced the most carbonate and carbonic oxide, that is to say, the following system:—

Equation (1) × ⅓ + eq. (2) × ⅛ + eq. (3) × ½.

We should have had in this case, for 120·8 grms. of matter, 815 Cal. and 363 litres of gas; or, for 1 kgm., 674·5 Cal. and 300·5 litres. These are practically the same figures as above.

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4. On the contrary, the transformations yielding the maximum of sulphate, that is to say, the following system:—

$$\text{Eq. (1)} \times \tfrac{7}{24} + \text{eq. (2)} \times \tfrac{1}{2} + \text{eq. (4)} \times \tfrac{1}{8} + \text{eq. (5)} \times \tfrac{1}{12},$$

should have produced, for 1238 grms. of matter, 853 Cal., and 321 litres of gas; or, for 1 kgm., 689 Cal. and 259 litres.

5. But the heat calculated as corresponding to the preceding transformations is greatly too small. In short, we neglected in the calculation—

1st. The change of the sulphide into trisulphide, which liberates about + 6 Cal. per equivalent.

2nd. The change of an appreciable portion of carbonic acid into bicarbonate, under the influence of a portion of the water (1 per cent.), contained in powder a reaction unnoticed in theoretical equations neglecting the presence of water.

This quantity, moreover, can hardly exceed 2 per cent.; that is to say, about an equivalent, being limited by the weight of the water itself as well as by the quantity of the latter, which produces sulphuretted hydrogen. Nevertheless this might add further + 12·4 Cal.

3rd. A portion of the sulphur, instead of producing potassium trisulphide, was changed into iron sulphide, which liberates per equivalent of sulphur—

$$F + S = FeS, + 11{\cdot}9 \text{ Cal.}$$

If the whole of the excess of sulphur assumed this form, we might therefore have a thermal excess of + 47·6 Cal., and even more, owing to the formation of a double iron and potassium sulphide. The real figure is lower, the sulphur being by no means all changed into iron sulphide, but it is impossible to determine it for want of data.

4th. The heat of combustion of carbon has here been calculated supposing it pure, and even in the diamond state. In reality the figure thus calculated is too low by an amount which may be regarded as compromised between 1·5 Cal. (pure carbon derived from charcoal) and 5·2 (bakers' embers), for 1 eq. (6 grms.) of carbon. This makes for 964 grms. of powder a thermal excess comprised between 31·5 Cal. and 109·2 Cal. It is true that this error is partly compensated, because we have taken the weight of real carbon as equal to the weight of charcoal, while it is less by about a fourth (see p. 488).

However this may be, we see from this that the error in the number above calculated (674·5 Cal.) might amount in an extreme case to—

$$109{\cdot}2 + 47{\cdot}6 + 12{\cdot}4 = 169{\cdot}2,$$

which would make in all 843·7 Cal., or an excess of a fourth in the number calculated.

The real excess, under the conditions of the experiment of

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Noble and Abel and the other authorities, is certainly less. But nothing can be definitely settled with regard to this point till a special study has been made of the heat of combustion of the charcoal used in the manufacture of each of the classes of powder which have been the object of the thermal measurements and the chemical analysis; as also the real proportion of the iron sulphide, and even of the double iron and potassium sulphide formed during combustion in the interior of an iron vessel.

6. *Heat liberated.* These reservations having been made, we shall give the figures found by the authorities who have measured the heat liberated by the combustion of powder in closed vessels. Bunsen and Schiskhoff found for 1 kgm., 619·5 Cal.; but this number, far lower than those of the other operators, appears to be invalidated by some error.

Roux and Sarrau found for 1 kgm. at constant volume in a bomb filled with air, of which the oxygen contributed to increase the heat liberated—

Cannon powder	753 Cal.
Fine sporting powder	807 „
B rifle powder	731 „
Powder of commerce	694 „
Blasting powder	570 „

Tromeneuc found from 729 to 890 Cal., viz.—

Ordnance powder	840 Cal.
English powder	891 „
Blasting powder	729 „

Noble and Abel gave at first (dry powder)—

RLG	696 to 706 Cal.
FG	701 to 706 „

mean, 705 Cal. They since discovered that these figures were slightly too low, and they supplied after correction the following new mean values:—

QUANTITIES OF HEAT LIBERATED BY THE COMBUSTION OF 1 GRM. OF POWDER SUPPOSED PERFECTLY DRY.

Pebble powder	721·4 Cal.
R.L.G., W.A. powder	725·7 „
F.G., W.A. powder	738·3 „
No. 6 Curtis and Harvey's powder ...	764·4 (733 to 784) Cal.
Blasting powder	516·8 Cal.
Spanish spherical	767·3 „

In order to be able to compare these figures with the numbers calculated, we must first take into account the ash, oxygen, and hydrogen contained in the charcoal, and, finally, the nitre which has escaped combustion. The weight of these various substances is properly known only for Noble and Abel's experiments. It amounts to about four per cent. of the weight of dry powder (more than one per cent. of moisture in ordinary powder).

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This being taken into account, the heat liberated amounts for 1 grm. of explosive matter really transformed to 750 Cal., a figure which exceeds by 75·5 Cal., or by a ninth, the theoretical value 674·5 Cal.

This excess is evidently owing to the causes just described, and principally to the use of charcoal instead of pure carbon, and to the formation of iron sulphide. The calculation made from the heat of combustion of the weight of pure carbon, as extracted from charcoal, would give 706 Cal., a value which is also too low. But the number 750 Cal. remains below the possible difference, which amounts to 843 Cal., according to what has been said above. For the powders studied by other observers, the effective reaction being unknown, we cannot carry out the thermal work with certainty. The values deduced from our equations generally remain below the figures actually found, which is attributable to analogous causes, and principally to the excess of heat produced by the combustion of the charcoal of powder. This excess will, moreover, vary with the constitution of this charcoal itself, which changes greatly in the different countries and for the different kinds of powder.

7. *Volume of the gases liberated.* The uncertainties are less, and consequently the discrepancies between theory and practice more limited for the volume of the gases. For instance, the volume of the gases obtained by Noble and Abel had a mean value of 267 litres, with variations comprised between 285 and 232 litres.

The following table, according to these authors, expresses the volume of the permanent gases produced by the explosion of 1 grm. of powder, supposed perfectly dry:—

W.A. pebble powder	278·3 c.c.
R.L.G., W.A. powder	274·2 „
F.G., W.A. powder	263·1 „
No. 6, Curtis and Harvey's powder	241·0 „
Blasting powder	360·3 „
Spanish spherical	234·2 „

Gay-Lussac assigned 250 c.c.[1] at a low pressure. Bunsen and Schiskhoff (sporting powder), 193 c.c. (at a low pressure); Linck, 218 c.c. (cannon powder) at high pressures; Karolyi, 209 c.c. (ordnance powder) and 227 c.c. (rifle powder); Vignotti, 231 c.c. to 244 c.c., according to the nature of the charcoal—results, the differences of which are attributable to the diversity of the pressures and relative proportions.

The above formula indicates 300 litres, a figure which would reduce itself to 288 litres were the foreign substances taken into account. The change of a small quantity of carbonic acid into bicarbonate would lower it still more, and bring it nearly to the value found by Noble and Abel.

[1] He gives elsewhere 449·5 cc., owing to some error in copying.

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8. The value of the permanent gases varies nearly inversely with the heat developed in accordance with the equation on p. 499 (see also p. 505), and as is shown by the table below—

Powder.	Heat disengaged per gramme of powder.	Volume of gases produced per gramme of powder.
Spanish pellet	767·3 Cal.	234·2 cc.
Curtis and Harvey No. 6	764·4 „	241·0 „
F.G., W.A.	738·3 „	263·1 „
R.L.G., W.A.	725·7 „	274·2 „
Pebble W.A.	721·4 „	278·1 „
Blasting	516·8 „	360·3 „

9. In general the characteristic product, QV, is nearly constant, as the author observed in 1871, for the various powders. Now, this product measures the strength for explosive substances of which the specific heat is the same, which is practically the actual case (p. 34).

The temperature of the combustion of powder has been estimated by writers on this subject, from rather uncertain tests, at 2200°.

10. The pressures developed during the combustion of powder at constant volume have been observed by Noble and Abel with the aid of the crusher. The following are their numbers :—

Density of charge $\frac{1}{n}$	Powder. Pebble and R.L.G.	F.G.
	Kgm.	Kgm.
0·1	231·3	231·5
0·2	513·4	513·4
0·3	829·4	539·4
0·4	1220·5	1219·0
0·5	1683·6	1667·8
0·6	2266·3	2208
0·7	3006·5	2883
0·8	3944·2	3734·1
0·9	5112	4786
1·0	6567	6066·5

These results may be represented, according to these authors, by the empirical formula, $\frac{2193}{n - 0{\cdot}68}$, or $\frac{2460}{n - 0{\cdot}6}$, formulæ in which they suppose that the products which are not gaseous at the temperature of the explosion occupy 0·68 c.c., or, more simply, 0·6, the same volume being calculated at the ordinary temperature.

The theoretical formula on p. 499 gives pressures nearly the same as the above for high densities of charge (1·0 and 0·9); below which it gives results which are too high, amounting to double the numbers found for the density 0·1. This difference increases as the pressure diminishes; it may be connected with the increase of dissociation.

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§ 8. Sporting Powder.

1. Sporting powder is distinguished from service powders principally by the surplus proportion of saltpetre and by the choice of the charcoal.

The following are the proportions adopted in France:—

Saltpetre	78
Sulphur	10
Charcoal	12

2. *The rapidity of inflammation* of sporting powder is less, according to Piobert, than that of service powder, being in proportion to the coarseness of the grains. For a sporting powder containing 30,000 grains to the gramme, the rapidity of the inflammation was 0·30 m. per second; while for a service powder containing 259 grains to the gramme, the rapidity amounted to 1·52 m.

The rapidity of combustion is also checked by the surplus proportion of saltpetre. It amounted to 8 mm. to 9 mm. per second in Piobert's experiments; while for service powder this writer found 10 mm. to 13 mm.

3. Brown charcoal tends to give powder shattering properties because it increases the heat liberated owing to the special composition of this charcoal.

4. The surplus proportion of saltpetre also increases the heat; but it diminishes the volume of the gases, as is shown by the figures on page 491, compared with those on page 503.

5. If the heat liberated be supposed proportional to the weight of the saltpetre, which should not be far from the truth, the heat will be greater by about a twenty-fifth for sporting, than for service powder, weight for weight. Now, the experimental data are not greatly at variance with this calculation. On the other hand, the permanent gases will diminish, which also agrees with Noble and Abel's results. Hence a certain compensation is afforded by it. Owing to this fact there is little difference between the strength of sporting and that of service powder.

§ 9. Blasting Powders.

1. Blasting powders present very varying proportions. The principal object aimed at is to increase the volume of the gases; which is attained by the diminution of the saltpetre, and the increase of the sulphur and charcoal. It is also sought to diminish the cost of this powder.

The following are the proportions adopted in France:—

Saltpetre	62
Sulphur	20
Charcoal	18

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In Italy:—

Saltpetre	70
Sulphur	18
Charcoal	12

What is called *export trade powder* in France, or *strong blasting powder*, contains—

Saltpetre	72
Sulphur	13
Charcoal	15

2. There was formerly distinguished a class known as *slow blasting powder*:—

Saltpetre	40
Sulphur	30
Charcoal	30

But the slowness of the reaction tended to diminish the effects too much, and this powder is no longer in use. However, this slowness may offer certain advantages for special uses, such as the making of flying fuses, composed in the following manner:—

Powder dust	25·0
Saltpetre	44·5
Sulphur	9·1
Wood charcoal	2·4

3. It was formerly supposed that blasting powder produces a much greater volume of gases than that of service powder, because it would be decomposed according to the following equation:—

$$2KNO_3 + 6C + S = 6CO + K_2S + 2N.$$

This equation would correspond to the proportions—

Saltpetre	65·5
Sulphur	10·0
Charcoal	24·5

But observation has proved that it must be rejected, at least as the fundamental representation of the reaction.

It would produce, moreover, so little heat (74·5 Cals. per kgm., p. 504), that the reaction could hardly propagate itself.

4. Now, powder with an excess of charcoal deflagrates with vivacity, and forms, like other powders, potassium sulphate and carbonate, with a liberation of heat which is probably not far remote from that of blasting powder for the same weight of nitre consumed. A portion of the carbon tends, however, to increase the proportion of carbonic oxide; but a considerable portion of the charcoal must remain intact.

5. Hence, in this case, as in the foregoing, the sudden transformation of the explosive substance has a tendency to form the products liberating the most heat, a remark of capital importance, and without which it would be difficult to understand

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the preponderating proportion of potassium sulphate and carbonate which is produced in every case. The production of potassium sulphide and carbonic oxide is due to the secondary reaction of the sulphur and charcoal on the above salts; it plays an essential part in the study of powder, as it contributes to increase the volume of the gases.

6. This being established, it may in general be admitted that the heat liberated by any powder is nearly proportional to the weight of saltpetre which it contains. The heat liberated by blasting powder will therefore be to that of service powder in the ratio of 62 to 75; Roux and Sarrau actually obtained 570 Cal. instead of 751 Cal.

7. Sarrau and Vieille since found the volume of the gases equal to 304 c.c. for French blasting powder at the density of charge 0·6.

This volume is greater by a tenth than that developed by service powder.

The pressures observed by them were—

Density of charge.	Pressure.
0·3	800 kgm.
0·6	2730 ,,

from which would result the pressure $\frac{4540}{n}$; a formula in which the volume of the solid substances is not taken into account.

8. These gases contained in 100 volumes—

CO_2	49·4
CO	20·5
H	2·0 to 1·4
CH_4	0·3 to 1·4[1]
H_2S	7·0 to 5·5
N_2O	21·3

The proportion of sulphuretted hydrogen is far larger than that for ordinary powder (4 per cent.).

The carbonic oxide forms a fifth of the volume of the gases, or 20 c.c., whilst with ordinary powder it amounts only on an average to one-eighth, viz. 12·5 c.c. Hence it will be seen that the volume of deleterious gases is nearly double, in the case of blasting powder, the volume of the same gases yielded by ordinary powder.

Noble and Abel found also 7·0 of sulphurettted hydrogen; but nearly equal volumes of carbonic oxide (33·7) and carbonic acid (32·1), which is still more disadvantageous. They obtained less heat and more gas with blasting than with service powder; which affords a compensation from the point of view of strength.

[1] The proportion of methane increases with the pressure (see p. 288 and 464).

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9. On the whole, blasting powder offers hardly any other advantage than its low price, due to the diminution in the weight of nitre. It would certainly be preferable to employ a less weight of ordinary powder, which would realise the same economy. Moreover, the daily increasing use of dynamite tends to limit the consumption of blasting powder.

§ 10. Powders with Sodium Nitrate Base.

1. Sodium nitrate lends itself as well as potassium nitrate to the manufacture of powders; it has been employed on a large scale in the Isthmus of Suez works, and offers a marked economy. It has also been employed in the mines of Freyberg and Wetzlar.

Unfortunately this salt is very hygroscopic, and the keeping of the powders into the composition of which it enters needs special precautions.

2. Thermal theories increase the interest there may be in overcoming these difficulties by showing that the powder with sodium nitrate base develops a greater pressure, weight for weight, than powder with potassium nitrate base, and that it can effect a greater work.

3. Take, in fact, a composition equal to that of powder, such as—

Saltpetre	75
Sulphur	10
Charcoal	15

It would correspond by weight to the following proportions:—

Sodium nitrate	71·8
Sulphur	11·3
Charcoal	16·9

4. Supposing the chemical reactions to be exactly the same, the heat liberated and the gaseous volume would also remain nearly the same at equal equivalents (p. 4). But at equal weights there would be, on the contrary, an eighth more heat, or for 1 kgm. 782 Cal. from the calculation (or 818 Cal. for carbon derived from wood charcoal), there would further be a volume of gas equal to 338 litres.

The resultant force would retain the same expression, but it would be increased by about an eighth for a given density of charge. Such are the results indicated by theory. But up to the present no experiment has been made to study the true reactions.

5. In general, powders with sodium base will develop stronger pressures and a greater quantity of heat, that is of work, than the same weight of powders with potassium base and of equivalent composition. Indeed, experiment proves that the substitu-

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tion of sodium for potassium in a defined salt, whether dissolved or anhydrous, causes an almost constant liberation of heat, whatever be the nature of the salt. Now, the alkaline metal existing in the saline form, both in the powder and in the products of combustion, its influence is eliminated in estimating the heat liberated by combustion, that is when the heat is estimated for equivalent weights of the sodium and potassium salts. Weight for weight, on the contrary, much more heat will be obtained with the sodium salts; similarly, a larger volume of gas will be obtained, since the equivalent of sodium is lower than that of potassium. Various explosives proposed for industrial purposes, such as Davy powder, pyronome,[1] Espir powder, may be classed with this one.

Take for example—

Sodium nitrate	63
Sulphur	16
Wood sawdust	23

This is a slow acting substance, employed in quarries, especially to produce dislocations. It is not explosive either by heating, ordinary shocks, or friction. It contains three to four per cent. of moisture, a quantity which may increase to as much as 30 per cent. by its being in a damp place, but not without the powder becoming deliquescent.

The following have been found as the tensions in a closed vessel:—

Densities of charge 0·4	1613 kgms.
„ „ 0·5	2401 „

values differing but slightly from that of ordinary blasting powder, which confirm the foregoing deductions.

7. The sodium nitrate powders have sometimes been mixed with dry sodium sulphate, or dried magnesium sulphate, to check the absorption of moisture. But the remedy is merely temporary, and of little efficiency.

The potassium and sodium, and even barium nitrates, have also been associated in the same explosive.

8. We shall further mention Violette's mixture:—

Sodium nitrate	62·5
Sodium acetate	37·5

This mixture corresponds to a total combustion—

$$10C_2H_3NaO_2 + 16NaNO_3 = 13CO_3Na_2 + 7CO_2 + 15H_2O + 16N.$$

The two salts may be melted together, which gives a very intimate mixture. But if the temperature be raised slightly

[1] Under the latter name variable mixtures containing as combustive elements the alkaline nitrate and potassium chlorate. This confusion should be avoided, the chlorate base powders being highly dangerous.

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above the melting point, the mixture explodes towards 350°. It is hygroscopic.

9. Lastly, the sulphur and carbon have been replaced by a compound which contains both, such as potassium ethylsulphocarbonate, or xanthate (xanthine powders)—

Saltpetre	100
Xanthate	40
Wood charcoal	6

§ 11. Powders with Barium Nitrate Base.

1. Barium nitrate has been introduced into the composition of the complex powders with special objects. The equivalent of this salt (130·5) being higher by nearly a third than that of potassium nitrate, it will be necessary to employ more of it. For instance, the following proportion—

Barium nitrate	80
Sulphur	8
Charcoal	12

will be equivalent to service powder.

2. With equivalent weight, always assuming the same chemical reactions, we should have nearly the same quantity of heat and the same gaseous volume. But it will be necessary to take a weight of powder greater by a little more than a fifth. Hence, weight for weight, the heat will be diminished by about a fifth, together with the volume of the gases and the strength, for a given density of charge.

3. The following mixtures, for example, have been proposed —lithofracteur, or saxifragine:

Barium nitrate	77
Wood charcoal	21
Potassium nitrate	2

Similarly the Schultze powders, a mixture of pyroxylated wood with potasium and barium nitrates (p. 459).

4. Barium nitrate is also employed in pyrotechny to produce green fires.

5. Strontium nitrate equivalent (105·7) differs but slightly from potassium nitrate. It is hardly employed, save in pyrotechny to produce red fires.

6. Lead nitrate equivalent (165·5) is capable of yielding for equal equivalents a fifth more oxygen than the other nitrates; but the reactions which it develops are by this very fact all different, since the lead is reduced to the metallic state, instead of subsisting under the form of carbonates, as happens with the alkaline nitrates. Besides, the high price of this substance, and its high equivalent, hardly permit of its being used, except for very special purposes; for instance, by mixing it with red phosphorus.

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CHAPTER XI.

POWDERS WITH CHLORATE BASE.

§ 1. General Notions.

1. Berthollet, after having discovered potassium chlorate, and recognised the oxidising properties so characteristic of this salt, thought of utilising it in the manufacture of service powders. He made several attempts in this direction, but immediately suspended them after an explosion which happened during the manufacture carried on at the Essonnes powder factory, an explosion in which several persons were killed around himself. The same attempt has been revived at various periods, with certain variations in the composition.

But in every case explosions, followed by loss of lives—such, for instance, as those which happened during the siege of Paris in 1870, and at L'École de Pyrotechnie in 1877—happened before long in the course of its manufacture.

It is thus clear that potassium chlorate is an extremely dangerous substance, which is only natural, because its mixture with combustible bodies is sensitive to the least shock or friction. The catastrophe in the Rue Beranger (see p. 46), produced by an accumulation of caps for children's play-things, containing potassium chlorate, has helped to confirm these ideas. Chlorate powders are, generally speaking, more easily ignited, and burn with more vivacity than black powder. They explode, like the latter, on contact with an ignited body. They are hardly used at the present day, except as fuses for fireworks, or to produce shattering effects in torpedoes, for instance. A powder of this kind has even been proposed in America as motive agent of forge-hammers or pile-drivers. In this case the cartridge is placed between the head of the pile and the ram, when the explosion drives in the one and sends the other upwards. Their strength is superior to that of nitrate base powders, but less than that of dynamite or gun-cotton.

2. We shall first state the general properties of chlorated

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compositions. Potassium chlorate, which is the essential ingredient, is a salt fusible at 334°, and which decomposes regularly at 352°. Nevertheless, it may become explosive by itself under the influence of a sudden heating, or a very violent shock (p. 406).

We have seen that it yields 39·1 per cent. of oxygen and 60·9 of chloride of potassium—

$$ClO_3K = KCl + O_3,$$

liberating, at the ordinary temperature, 11 Cal. for each equivalent of oxygen (8 grms.) fixed; or 1·4 Cal. per gramme of oxygen; or 0·54 Cal. per gramme of potassium chlorate.

These quantities of heat must therefore, generally speaking, be added to those which would be produced by free oxygen, when developing the same reaction at the expense of a combustible body (p. 134). But the presence of the potassium chloride, which acts as inert matter, tends to lessen this advantage.

3. The extreme facility with which potassium chlorate powders explode under the influence of the least shock is a consequence of the great quantity of heat liberated by the combustion of the particles which are ignited at the very outset and their low specific heat; this heat raises the temperature of the neighbouring portions higher in the case of chlorate than of nitrate powder, and it therefore more easily propagates the reaction. The influence is the more marked the lower the specific heat of the compounds,[1] and as the reaction commences, according to the known facts, at a lower temperature with the chlorate than with the nitrate of potassium.

Everything, therefore, combines to render the inflammation of the powder with chlorate base easier.

Therefore the substances of which they are formed should not be pulverised or crushed together, but pulverised separately and mixed by screening.

The drying in the stove of these powders is dangerous. The presence of powdered camphor, so efficacious with gun-cotton, does not lessen the sensitiveness of chlorate powders.

4. Not only is the chlorate powder more energetic and inflammable, but its effects are more rapid; it is a shattering powder. Theory again is able to account for the property. In fact, the compounds formed by the combustion of chlorate powder are all binary compounds, the simplest and most stable of all, such as potassium chloride, carbonic oxide, and sulphurous acid. Such compounds will undergo dissociation at a higher temperature and in a less marked manner than the more com-

[1] In fact, these two powders only differ by the substitution of the chlorate, the specific heat of which is 0·209, for the nitrate, the specific heat of which is 0·239.

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plex and advanced combinations, such as potassium sulphate and carbonate, or carbonic acid, which are produced by nitrate powder. It is for this reason that the pressures developed in the first instance will be nearer the theoretical pressures with chlorate than with nitrate powder, and the variation in the pressures produced during the expansion of the gases will be more abrupt, being less checked by the action of the combinations successively reproduced during the cooling.

5. The explanations just given apply not only to powders in which potassium chlorate is mixed with charcoal and sulphur, compared with analogous powders with nitre as base, but also comprise all powders formed by the association of the same salts with other substances. It can be shown that this is so, without entering into special calculations, for which the exact values would in the majority of cases be wanting.

Now, our comparisons are based on the following data, which present a general character:—

1st. Both salts employed in equal weights supply to the bodies which they oxidise the same quantity of oxygen. 122·6 grms. of chlorate yield 6 equiv. or 41 grms. of oxygen; that is to say, 8 grms. of oxygen for 20 grms. of chlorate; whilst 101 grms. of potassium nitrate yield only 5 equiv., or 40 grms. of available oxygen, viz. 8 grms. of oxygen to 20·2 grms. of salt. Hence it follows that both salts must be employed in equal weights in the greater number of cases.

Now, one and the same weight of oxygen, 8 grms., yielded by potassium chlorate liberates + 11 Cal. more than free oxygen; if it be yielded by the nitrate, it produces on the contrary + 8·3 Cal. less;[1] which makes a difference of 19·3 Cal., or 6·95 Cal. per gramme of salt employed.

The formation of the same compounds will therefore liberate more heat with the chlorate than with the nitrate, and the excess will subsist, even in taking into account the union of the acids of sulphur and carbon with the potash of the nitrate.

This greater quantity of heat will give rise to a higher temperature, since the mean specific heat of the products is less with the chlorate than the nitrate. The mean specific heat of the products at constant volume may be calculated theoretically by multiplying the number of atoms by 2·4, and dividing the product by the corresponding weight. Now, the weight of the combustible body being the same will require the same respective weights of nitrate and chlorate, according to what has just been said; but the latter will correspond to a less number of atoms, since the equivalent of chlorine is greater than that of nitrogen.

2nd. The volume of the permanent gases is greater, or at the

[1] Supposing it to act upon a carbonated body, the carbon of which is changed into potassium carbonate.

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lowest equal, with potassium chlorate than with the nitrate, because the potassium of the former salt remains in the form of chloride, the whole of the oxygen acting on the sulphur and carbon to produce gases; whereas the potassium of the nitrate retains a part of the oxygen, at the same time as it brings a portion of the sulphur and carbon to the state of saline and fixed compounds, the formation of the salts more than compensating for the volume of nitrogen set free.

3rd. In the case where only the carbon or a hydrocarbon burns, the compensation in the gaseous volumes is exactly effected because each volume of nitrogen liberated from the nitrate replaces an equal volume of carbonic acid combined with the potassium yielded by the said nitrate. Nevertheless the pressure will be increased, even in this case, with the chlorate, because its temperature is higher.

4th. The compounds formed with the chlorate being in general simpler than with the nitrate, dissociation will be less marked, and consequently the action of the pressures will be at once more extended, because the initial pressure is greater, and more abrupt, because the state of combination of the elements varies between narrower limits. Hence arise shattering effects rather than those of dislocation or projection.

6. Potassium chlorate possesses another property which has sometimes been utilised. Its mixture with organic substances, or with sulphur or other combustible bodies, takes fire under the influence of a few drops of concentrated sulphuric acid; which is due to the formation of chloric acid, which is immediately decomposed into hypochloric acid, an extremely explosive compound and a very powerful combustive.

This property has been utilised to cause the ignition by shock of torpedoes and hollow projectiles charged with potassium chlorate powder. It is sufficient to place in them a tube or glass balls, filled with concentrated sulphuric acid.

This artifice may even be employed to ignite chlorate fuses for exploding dynamite or gun-cotton.

But all these arrangements are very dangerous for those who put them into execution, and they have not been practically adopted.

7. We have yet to say a few words about *potassium perchlorate*, which is generally regarded as equivalent to the chlorate, but by a mere theoretical generalisation, for it is a salt which is expensive, difficult to prepare pure, and it has hardly formed the object of real experiments as an explosive agent.

Weight for weight it yields a little more oxygen than the chlorate; about a sixth, viz. 46·2 per cent. instead of 39·1.

$$ClO_4K = KCl + O_4.$$

But this liberation of oxygen absorbs heat; − 7·5 Cal. per

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equivalent of salt, or − 0·9 Cal. per equivalent of oxygen, instead of liberating it.

From this point of view, therefore, the perchlorate acts almost like free oxygen, with the disadvantage of half of it being useless inert matter.

Pure perchlorate is not explosive either by shock or inflammation, as the chlorate. Further, its mixtures with organic substances are far less sensitive to shock, friction, the action of acids, etc. They ignite with more difficulty and burn slower.

§ 2. Chlorated Powders properly so called.

1. Potassium chlorate powder was formerly manufactured in the following proportions:—

Chlorate	75·0
Sulphur	12·5
Charcoal	12·5

This powder is extremely shattering and easy to ignite; its preparation has occasioned terrible accidents, but the true reaction which it develops is not well known. The above proportions correspond to the following weights:—

$$3ClO_3K + 2S + 5C,$$

assuming the weight of pure carbon equal to that of charcoal, which however is not exact (see p. 488).

It was first supposed that the reaction consists in the transformation of this system into the following bodies:—

$$3KCl + 2SO_2 + 5CO.$$

The presence of sulphurous acid is unquestionable at any rate, but carbonic acid is also produced, which the equation does not take into account.

The same uncertainty prevails concerning the numberless mixtures formed by potassium chlorate, whether pure or mixed with nitrate, these bodies being associated with combustible substances, such as charcoal, sugar, ferrocyanide, tan, wood sawdust, gamboge, benzene, sulphur, carbon disulphide, antimony sulphide, and the metallic sulphides, phosphorus and the phosphides, etc., all these being mixtures which have been proposed or patented of late years, both as explosives and fuses. We shall give the theoretical calculations only for the total combustion mixtures formed by the association of potassium chlorate with carbon, sulphur, sugar and yellow prussiate, for the sake of comparison between them, and the analogous mixtures formed by potassium nitrate.

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2. Take first the chlorate mixed with carbon supposed pure—

$$2ClO_3K + 3C = 3CO_2 + 2KCl.$$

The equivalent weight is 140·6 grms., and there is formed 66 grms. carbonic acid and 74·6 potassium chloride, which makes for 1 kgm. 872 grms. chlorate, 128 grms. carbon, with the production of 469 grms. carbonic acid.

The heat liberated amounts to + 152 Cal. at constant pressure, + 153·5 at constant volume; or, for 1 kgm., 1010 Cal. at constant pressure, 1092 at constant volume.

Reduced volume of the gases, 33·5 litres; or, for 1 kgm. 238 litres.

$$\text{Permanent pressure} = \frac{238 \text{ atm.}}{n - 0{\cdot}27}, \text{ with the usual reservation.}$$

$$\text{Theoretical pressure} = \frac{5950 \text{ atm.}}{n - 0{\cdot}27}.$$

3. Take again *chlorate mixed with sulphur*—

$$2ClO_3K + 3S = 3SO_2 + 2KCl.$$

This mixture ignites at 150°.

The equivalent weight is 170·6 grms., and there is formed 96 grms. sulphuric acid and 74·6 grms. potassium chloride. This makes for 1 kgm. 719 grms. chlorate, 281 grms. sulphur, with the production of 563 grms. sulphurous acid. The heat liberated amounts to 124·8 Cal. at constant pressure, 126·3 at constant volume; or, for 1 kgm., 731 Cal. at constant pressure, 740 Cal. at constant volume.

Reduced volume of gases, 33·5 litres; or, for 1 kgm., 196·4 litres.

$$\text{Permanent pressure} = \frac{196{\cdot}4 \text{ atm.}}{n - 0{\cdot}22}, \text{ with the usual reservation.}$$

$$\text{Theoretical pressure} = \frac{4120 \text{ atm.}}{n - 0{\cdot}22}.$$

4. *Chlorate mixed with equal weights of sulphur and carbon* (total combustion)—

$$22ClO_3K + 9S + 24C = 9SO_2 + 24CO_2 + 22KCl.$$

The equivalent weight is 1637 grms. and there is formed 288 grms. sulphurous acid, 528 grms. carbonic acid, and 821 grms. potassium chloride; which makes for 1 kgm. 824 grms. chlorate, 88 grms. sulphur, 88 grms. carbon, with the production of 176 grms. sulphurous acid and 322 grms. carbonic acid.

The heat liberated amounts to 1560 Cal. at constant pressure, 1576 at constant volume; or, for 1 kgm., 953 at constant pressure, 963 at constant volume.

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Volume of the gases, 368 litres; or, for 1 kgm., 225 litres.

$$\text{Permanent pressure} = \frac{225 \text{ atm.}}{n - 0{\cdot}25}, \text{ with the usual reservation.}$$

$$\text{Theoretical pressure} = \frac{5170 \text{ atm.}}{n - 0{\cdot}25}.$$

5. *Chlorate mixed with cane sugar*—

$$8ClO_3K + C_{12}H_{22}O_{11} = 12CO_2 + 11H_2O + 8KCl.$$

The equivalent weight is 661 grms. There is formed 264 grms. carbonic acid, 99 grms. water, and 298 grms. chloride, which makes for 1 kgm. 742 grms. of chlorate, 258 grms. sugar, with the production of 400 grms. carbonic acid, 150 grms. water.

Heat liberated: + 766 Cal. liquid water[1] at constant volume, + 726 Cal. gaseous water; or, for 1 kgm., 1159 Cal. liquid water, 1098 Cal. gaseous water.

Volume of the gases, 134 litres liquid water, 257 litres gaseous water.

$$\text{Permanent pressure} = \frac{134 \text{ atm.}}{n - 0{\cdot}23}, \text{ with the usual reservation.}$$

$$\text{Theoretical pressure} = \frac{5400 \text{ atm.}}{n - 0{\cdot}23}.$$

6. Chlorate mixed with potassium ferrocyanide (yellow prussiate), supposed dry—

$$46KClO_3 + 9K_4FeC_6N_6 = 36CO_2 + 18K_2CO_3 + 54N + 3Fe_3O_4 + 46KCl.$$

This makes by weight, 1880 grms. of chlorate and 1105 grms. prussiate; in all, 2985 grms.; or, for 1 kgm., 630 grms. chlorate and 370 prussiate.

There is formed 528 grms. carbonic acid, 828 grms. carbonate, 232 grms. nitrogen, and 323 grms. magnetic oxide.

The heat liberated amounts to 2700 Cal. at constant pressure, 2711 Cal. at constant volume; or, for 1 kgm., 904 Cal. at constant pressure, 908 Cal. at constant volume.

Volume of the gases, 468 litres; or, for 1 kgm., 157 litres.

$$\text{Permanent pressure} = \frac{157 \text{ atm.}}{n - 0{\cdot}34}, \text{ with the usual reservation.}$$

$$\text{Theoretical pressure} = \frac{3120 \text{ atm.}}{n - 0{\cdot}34}.$$

7. We shall first compare with each other the results

[1] Neglecting the dissolving action of the water on the chloride.

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obtained by the total combustion of various bodies by potassium chlorate.

	Weight of the chlorate.	Heat liberated by 1 kgm. of the mixture.	Gaseous volume.	Theoretical pressure.
		Cal.	Litres.	
Chlorate and carbon	872	1092	238	$\frac{5950}{n - 0{\cdot}27}$
Chlorate and sulphur . . .	719	740	196	$\frac{4120}{n - 0{\cdot}22}$
Chlorate with sulphur and carbon	834	963	225	$\frac{5170}{n - 0{\cdot}25}$
Chlorate and sugar	742	726	257 [1]	$\frac{5400}{n - 0{\cdot}23}$
Chlorate and prussiate . . .	630	931	157	$\frac{3120}{n - 0{\cdot}3}$

From this we see that the mixture of chlorate and carbon is the most advantageous, weight for weight; but that the mixture of chlorate and sugar develops a nearly equal pressure, with a relative weight of chlorate less by a seventh. The mixture of chlorate and prussiate is not advantageous, the iron acting as an almost useless inert component, that is to say liberating a relatively small amount of heat.

8. Let us now examine the results obtained with chlorate and the analogous data relating to the mixtures formed by saltpetre, for equal weights, such as 1 kgm. of the mixtures, always considering total combustion.

	Heat.	Volume of the gas.	Theoretical pressure.
	Cal.	Litres.	
Chlorate and sulphur	740	196	$\frac{4120}{n - 0{\cdot}27}$
Nitrate and sulphur	653	168	$\frac{2550}{n - 0{\cdot}25}$
Chlorate and carbon	1092	232	$\frac{5950}{n - 0{\cdot}22}$
Nitrate and carbon	786	245	$\frac{3430}{n - 0{\cdot}27}$
Chlorate, sulphur, and carbon . . .	963	225	$\frac{5400}{n - 0{\cdot}25}$
Nitrate, sulphur, and carbon	801	111	$\frac{2060}{n - 0{\cdot}12}$

[1] Gaseous water.

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It will be seen that in general the values for the chlorate base powders are much greater than those for the corresponding nitrate base powders.

The pressures exerted by the former are greater, for the two-fold reason that the quantities of heat developed are greater, and the gaseous volumes equal or greater. Hence these powders will produce effects, both of dislocation and projection, superior to those of the nitrate base powders.

These conclusions agree perfectly with the known facts, and it seems that they may be extended to incomplete combustion powders.

But, on the other hand, all the numbers given are far inferior, with regard both to heat and gaseous volume, to those of gun-cotton and dynamite (pp. 425 and 451). This inferiority will not disappear, even for the greatest gaseous volumes which result from incomplete combustion.

From this point of view, therefore, the chlorate powders do not exhibit any superiority over the new explosive substances sufficient to compensate for the exceptional dangers in manufacturing and handling them. It is only as fuses that their easy inflammation may offer certain advantages.

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CHAPTER XII.

CONCLUSIONS.

We have now reached the end of our task. We have submitted a general theory of explosive substances, based on the knowledge of their chemical metamorphoses, and of the heat of formation of the compounds which contribute thereto, that is to say, entirely deduced from thermo-chemistry. We will summarise the fundamental results of this study, both as regards general notions and as regards the particular definition of explosive bodies.

Meanwhile, industry, in this respect, as in many others, has received an unexpected impetus as a consequence of the theoretical discoveries of organic chemistry; discoveries which have facilitated the manufacture at will of a multitude of explosive substances hitherto unknown, and whose properties vary *ad infinitum*.

Empiricism, however, was still the only guide in forecasting with accuracy the properties of each of these substances at the time when thermo-chemistry came to our aid, enabling us to establish the general principles which define new explosive substances according to their formulæ and their heat of formation. Thermo-chemistry thus marks the limits which we can hope to reach in practice, and it lends the light of rational rules, by which alone the subject is capable of being fully developed.

It is this transformation of the empirical study of explosive substances into a strict science, based on thermo-chemistry, that the author has been pursuing since 1870, and of which the present work is the most advanced expression at the present state of our knowledge.

§ 1. Summary of the Work.—Book I.

1. The sudden development of a considerable expansive force characterises explosive substances. By this means they effect enormous mechanical work, which industry would be unable to

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accomplish otherwise, except by the aid of complicated, bulky machinery, necessitating considerable hard labour and expenditure. By this means also we have replaced with unspeakable advantage the energy afforded by the old war appliances based on the use of the lever and the sling, while at the same time the range and the power of the new weapons are extended far beyond the dreams of former days.

Such mechanical effects are produced by the act of explosion and by the energy of gaseous molecules, and even this energy results from chemical reactions, these latter, in fact, determining the volume of the gases, the quantity of heat, and consequently the explosive force.

2. Two orders of effects should here be distinguished: the one due to pressure, the other to the work developed. Thus the rupture of hollow projectiles and the dislocation of rocks is due more especially to pressure; whereas the clearing away of materials in mines and the projection of missiles in firearms represent more especially work due to expansion. Now, pressure depends both on the nature of the gases formed and on their volume and temperature. Work, on the contrary, depends especially on the heat liberated, which is the measure of the potential energy of the explosive substance.

The time necessary for the realisation and the propagation of chemical reactions plays an essential part in the applications, as the terms shattering powders, slow powders, and rapid powders themselves indicate. These various characters do not depend merely on the structure of the powders and of the nature of the reactions; but we may observe, even with the same explosive substance, taken in an identical form, extremely unequal durations of combustion, and consequently of its effects.

This, for instance, is what is exemplified in dynamite. Such diversities are observable in a substance which is identical in its chemical composition and in its physical structure. They result from the establishment of two very different laws: the law of ordinary combustion slowly communicated, and the law of detonation, that is to say, the law of the explosive wave which propagates itself with a lightning-like velocity.

These notions on the velocity of the propagation of phenomena, added to the knowledge of the heat liberated and of the volume of gases, characterise the comparison which may be made between the old black powder and the new substances now practically used, such as dynamite and gun-cotton.

From this it follows that, in order to define the force of an explosive substance, we should know the following data: first, the nature of the chemical reaction which determines the heat developed and the volume of gases, and secondly, the rapidity of the reaction.

3. Chemical reaction is characterised by the initial composi-

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tion of the explosive substance and by the composition of the products of explosion. These are further defined, *à priori*, in the case of a total combustion, that is to say, when the substance contains a sufficient quantity of oxygen. This is the case with nitroglycerin and nitromannite, where carbon and hydrogen are entirely transformable into water and carbonic acid.

If, on the other hand, oxygen be deficient, the products vary with the conditions, and several reactions are often produced simultaneously, as is the case with ammonium nitrate, with gun-cotton, and also with service powder. This last, for instance, does not only produce carbonic acid, potassium sulphate, and carbonate, the results of a complete explosion, but also carbonic oxide and potassium sulphide, due to an imperfect reaction.

In both cases it must be borne in mind that the products developed at the moment of the explosion, and at the high temperature of such explosion, are not necessarily the same as the products observed after cooling. A part of the water, for instance, may be found decomposed into oxygen and hydrogen, a part of the carbonic acid into oxygen and carbonic oxide. Such are the effects of dissociation; it tends to diminish the pressure of the system at the moment of the explosion, owing to the lesser amount of heat developed, but heat is regenerated, even during the process of cooling; and it is this which moderates the expansion and brings the total amount of work to the same value as if dissociation had not taken place.

4. The liberated heat is calculated from our knowledge of the products of the reaction, either under constant pressure or under constant volume; it is calculated, that is, if the reaction is not accompanied by any mechanical work. Otherwise, there is a transformation of a part of this heat into work. Now, it is precisely this transformation which it is proposed to effect by the use of explosive substances. It never takes place except fractionally, as we see in all transformations of this kind in mechanics. The fraction available in principle amounts almost to one-half in ordinary gunpowder; in practice we have not obtained more than one-third. This figure defines the maximum results which have been observed for this substance, constantly employed in artillery.

5. The volume of gases also results from chemical reaction; it is easily found from the equation which expresses this reaction. It may be calculated either at a temperature of 0°, and under normal pressure, or at any temperature or pressure. It should be observed that in making this calculation it is necessary to add to the permanent gases the volume of the bodies, such as water or mercury, which are susceptible of acquiring the gaseous stage at the explosive temperature. Water, in fact,

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hardly plays any part in the case of service powder, which barely contains one per cent. of its weight of water; but water is, on the other hand, a very important factor in gun-cotton, nitroglycerin, and in the majority of organic explosive substances.

6. Having thus defined the volume of the gases we deduce from it the pressure which they should exercise at the temperature developed by the explosion at constant volume, and even at any volume. This calculation rests on the ordinary laws of gases, laws whose application to these conditions requires the greatest caution. Thus it is preferable, in practical application, to measure the pressure of the gases direct from some of their given mechanical effects, and particularly from the crushing of small copper or leaden cylinders.

The results should be referred to the weight of the water contained in the unit of volume. Now, experience shows that the pressure of the unit of weight for the unit of volume tends to a constant value; this is what we term specific pressure, and this can be taken as a certain measure of force. Here we may note a remarkable circumstance: the pressures found by experiment are similar to the figures calculated by the ordinary laws of gases, whether for solid or liquid explosive compounds; at least, for those which, in becoming transformed, give rise to products which cannot be dissociated, such as nitrogen sulphide and mercury fulminate.

On the other hand, in the case of gaseous explosive mixtures, systems whose density for the unit of volume is low, we find a considerable difference ranging from the single to the double, and even beyond this. This difference may be attributable either to dissociation, or to uncertainty as to the real laws of gases, which would be applicable under these extreme conditions.

The maximum effort of an explosive substance evidently applies to that case in which it explodes in its own volume. Owing to this the effect will be all the greater in proportion to the density of the substance. Such is the circumstance which, added to the suddenness of the chemical decomposition, appears to confer on mercury fulminate the pre-eminence over all other bodies used as primings. The density of the fulminate is, in fact, almost five times as great as that of nitroglycerin. This allows mercury fulminate to exercise an effort which seems to attain 27,000 kgm. per square centimetre, being almost triple the effort exercised by the other known substances.

Here we have the total consequences deducible from the mere knowledge of chemical reaction. But in order to completely define an explosive substance it is also desirable to know, as we have said above, what is the duration of its transformation.

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7. This is a new datum in the problem, and one of the most important, since it determines the real effects of explosive substances in their various applications, such as the velocity communicated to projectiles in fire-arms, the division and the projection of fragments of bombshells, and, in fine, the various results developed in blasting at the expense either of the rocks required to be dislocated or removed, or of any obstacles which it is proposed to crush or overturn.

8. The origin of explosive reactions, that is to say, of the preliminary work which determines their beginning, appears to correspond in all cases to an initial heating, which raises the substance to its decomposing temperature, and from which reaction propagates itself. In order for this heating to be efficacious, the heat developed by the decomposition must attain a sufficient intensity to raise gradually, and up to the same degree, the temperature of the adjacent portions; it is necessary, also, that the heat should not become dissipated meanwhile by radiation, by conduction, or by the expansion of the compressed gases. In other words, the molecular velocity of the reaction in the system regarded as homogeneous, and raised to a uniform temperature throughout, must be sufficiently great, otherwise there would be no explosion. This is noticeable when decomposing cyanogen by means of the electric spark, or when changing acetylene into benzene by heating. The heat liberated by this last reaction is enormous, and for equal weights is four times that of the explosion of gunpowder, but it is so slowly disengaged that dissipation takes place gradually.

9. The molecular velocity of a reaction is therefore a main element in the question. Let us summarise the laws which characterise it.

It increases with the temperature according to a very rapid law.

It increases also with the condensation of the substance, that is to say, with the pressure in the gaseous systems.

On the other hand, its action is retarded by the presence of an inert body which lowers the temperature at the same time as it lessens condensation. In this way we can at will modify the character of an explosive substance. For instance, black powder, mixed with sand, will fuse instead of detonating; dynamite, which is a mixture of silica and nitroglycerin, is less shattering than nitroglycerin; besides, the shattering character due to the nitroglycerin decreases rapidly in proportion as the quantity of silica is increased.

10. The velocity of the propagation of reactions developed in consequence of ignition or of a local shock, represents a phenomenon totally distinct from the molecular velocity which we have just defined; for it expresses the requisite time for the physical conditions of temperature, etc., which have caused the

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phenomenon at one point to reproduce themselves successively at all points of the mass. This is what has been illustrated by the works of artillerists on the velocity of the combustion of ordinary powder, a velocity which is variable with the physical structure of powders and their chemical composition. This velocity varies exceedingly with the pressure; gunpowder, for instance, does not explode in a vacuum, because the heated gases which combustion has caused, escape, and are dispersed before having had time to communicate the heat to the adjacent particles.

Here considerations of an entirely novel character intervene.

Formerly, it was thought it was sufficient to inflame an explosive substance, no matter how, since the effects of the ensuing explosion did not appear to depend on the initial process of inflammation. But nitroglycerin and gun-cotton have manifested a peculiar diversity in this respect. Thus, for instance, according to the process employed in ignition, dynamite can decompose quietly and flamelessly, or it may burn with a flame, or again, it may give rise to explosion properly so called; this explosion may further be either moderated or accompanied by shattering effects. Mercury fulminate used as a priming is particularly apt to cause these latter effects; it is the detonating agent *par excellence*.

11. It has been shown how thermo-dynamic theories and the suitable analysis of the phenomena of shock will explain this diversity; the energy of the shock transforming itself into heat at the point acted on, and raising the temperature of the parts first struck, up to the degree of explosive decomposition, their sudden decomposition produces a fresh shock more violent than the first on the adjacent parts; and this regular alternation of shocks and of decompositions transmits the reaction from layer to layer throughout the whole mass, developing a real explosive wave, which progresses with a velocity incomparably greater than that of simple inflammation.

12. By this we see the all-importance of primings, hitherto looked upon as simple igniting agents. Here also we note the distinction between progressive combustion and the almost instantaneous detonation of explosive substances, extreme phenomena among which we observe a series of states and of intermediate reactions, which explain the variety of the effects produced by the same agent. In fact, there exists in chemistry a certain number of endothermal combinations, that is to say, those which are susceptible of liberating heat by their decomposition; these are acetylene, cyanogen, and arseniuretted hydrogen, etc. Yet these gases do not detonate either by heating or by the electric spark. The author has now shown that these same gases do, on the contrary, detonate and resolve themselves into elements, and with peculiar violence, under the influence of

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the sudden shock produced by the explosion of mercury fulminate.

13. Hence we are led to account for explosions by influence, peculiar phenomena which have singularly attracted the attention of artillerists and engineers.

It has been seen, for instance, that a cartridge of dynamite or gun-cotton, exploded by means of a fulminate priming, causes the explosion of the neighbouring cartridges even when placed at considerable distances, and without the detonation being followed by a direct propagation of the inflammation. Torpedoes charged with gun-cotton and submerged will also explode under the influence of strong cartridges of the same agent placed in the vicinity. In the present work it has been shown how these phenomena explain themselves by the development of the explosive wave in the detonating substance, and by the violence of the sudden shock which results therefrom, and which the surrounding medium transmits to the second cartridge.

Here is recalled to mind, though the author does not adopt it, the ingenious theory of synchronous vibrations, according to which the determining cause of the detonation of an explosive body consists in the synchronism between the vibrations of the body which causes the detonation and that which would be produced by the body acted upon. It is shown that this theory does not in reality explain the facts observed, and the chemical stability of matter in sonorous vibration is proved by direct experiment; these experiments have been made with the most unstable substances, such as ozone, arseniuretted hydrogen, persulphuric acid, oxygenated water, etc.

The sonorous waves, properly so called, are not therefore the real agents propagating chemical decompositions and explosions by influence; their energy and their pressure are too slight to provoke such effects. But propagation takes place in consequence of the explosive wave, a phenomenon of quite a different nature, and in which the pressure and energy are incomparably greater, and are incessantly regenerated throughout the wave by chemical transformation itself.

Thus, according to the new theory, explosive matter detonates by influence, not because it transmits the initial vibratory movement by vibrating in unison, but, on the contrary, because it stops it and appropriates to itself the energy thereof.

14. Let us examine somewhat more closely the characteristics of this explosive wave which we have been led to discover, and of which we avail ourselves, in order to explain the detonations of dynamite and gun-cotton. Its discovery, as well as the study of it, constitute one of the most interesting chapters in the present work.

It is in gaseous media that the study of it is at one and the

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same time the easiest and the strictest, and it is then that the results it offers are most far reaching, theoretically speaking. This study enables us, in fact, to show the existence of a new kind of undulatory movement of a compound order, that is to say, produced in virtue of a certain concord of physical and chemical impulses, within a substance under transformation. In the sonorous wave the energy is weak, the excess of pressure stands at the minimum, and the velocity is determined by the mere physical constitution of the vibrating medium. On the other hand, it is the change in the chemical constitution which propagates itself in the explosive wave, and which communicates to the system an enormous energy and considerable excess of pressure. Like phenomena may become developed both in solids and in liquids.

This wave propagates itself uniformly with a velocity depending essentially on the nature of the explosive mixture, and which is almost independent of the diameter of the tubes, except when these latter are capillary. It is equally independent of pressure, a fundamental property which determines the general laws of the phenomenon.

Finally, the energy of the translation of the molecules of the gaseous system produced by the reaction, and containing all the heat developed by such reaction, is in proportion to the energy of the gaseous system itself, containing merely the heat which it retains at zero. This is an essential detail which experience has confirmed, and which enables us to calculate the velocity of the explosive wave in the most diverse mixtures.

It appears that in the act of explosion a certain number of gaseous molecules among those which form the inflamed sections at the outset, are hurled forward with all the velocity corresponding to the maximum temperature developed by the chemical combination. Their shock determines the propagation of this latter through the neighbouring sections, and the movement is reproduced from section to section with a velocity which may be compared to that of the molecules themselves.

It is in this way that observations were made of the propagations of explosions, with velocities of 2480 metres per second in a mixture of oxygen and hydrogen, of 2480 metres in a mixture of oxygen and acetylene, and of 2195 metres in a mixture of cyanogen and oxygen, etc. This velocity constitutes a genuine specific constant for every gaseous mixture.

The propagation of the explosive wave is a phenomenon altogether distinct from ordinary combustion. It only occurs when the inflamed section exercises the greatest possible pressure on the adjoining section; that is to say, when the inflamed molecules preserve almost in its entirety the heat developed by chemical reaction. This state constitutes the law of detonation.

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On the other hand, the law of ordinary combustion answers to a system in which heat is to a great extent lost by radiation, conduction, expansion, contact with surrounding bodies, etc., with the exception of the very small quantity indispensable for raising the adjacent parts up to the temperature of combustion; the excess of heat here tends to reduce itself to zero, and consequently the excess of the velocity of translation of the molecules, that is to say, the excess of pressure of the inflamed section on the adjacent section.

After having shown in Book I. the general characteristics of explosive phenomena, it is now desirable to define the fundamental circumstance which determines their energies, that is, the heat liberated by chemical transformation. This is the object of Book II.

Book II.

Any theoretical study of explosives demands a general knowledge of the principles of thermo-chemistry, namely, of its methods and of its results; we have deemed it fitting to summarise these notions at the opening of Book II. The reader will there find more especially the description of the author's ordinary calorimeter and of the calorimetric bomb which he used in studying the heat of detonation of a large number of gases. Some extensive tables will be shown in this summary, showing the heat of formation of the principal combinations in various stages, as also the specific heats and densities of the various compounds likely to intervene in the study of explosive substances.

We have devoted ourselves principally to the heat of formation of those fundamental compounds which help to form these substances, namely, oxygenated compounds of nitrogen and their salts, the hydrogenated compounds of nitrogen, cyanic compounds, carbonated derivatives of nitrogen, nitrogen sulphide, hydrocarbon nitric derivatives, such as nitric ether of alcohol, nitroglycerin, nitromannite, gun-cotton; the nitrated derivatives, such as nitro-benzene, picric acid, etc.; the azoic derivatives, such as diazobenzene and mercury fulminate. We have also studied the results derived from the oxacids of chlorine and the explosive oxalates.

This study, which has been lengthy, difficult, and sometimes even fraught with danger, is almost entirely the result of the author's own personal experiments.

Hence it has been thought advisable to set down here the amplified statement of methods and results, and thus to place before the readers all the data on which the thermo-chemistry of explosive compounds is based.

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Book III.

1. It now remains merely to define the force of the various explosive matters, regarded individually, in accordance with the general principles set down in the first two portions of the work. This is the object of Book III.

2. In practice, a system susceptible of a rapid transformation, accompanied by a marked development of gas and by great development of heat, may be utilised as an explosive agent. These systems belong, in fact, to eight distinct groups, namely:—

The explosive gases (ozone, oxacids of chlorine) formed with absorption of heat, that is to say, containing an excess of energy (acetylene, cyanogen, etc.).

Detonating gaseous mixtures—such as hydrogen, carbonic oxide, and hydrocarbons, mixed with oxygen, chlorine, and oxides of nitrogen.

Explosive mineral compounds — nitrogen sulphide and chloride, fulminating metallic oxides, ammonium nitrate, etc.

Explosive organic compounds—nitric ethers, nitric derivatives of hydrocarbons, nitro derivatives, diazoic derivatives, fulminates, perchloric ethers, salts of metallic oxides easily reducible.

The mixtures of explosive compounds with inert bodies.

The mixtures formed by an explosive oxidisable compound and a non-explosive oxidising body—gun-cotton mixed with nitrate, picrate mixed with chlorate, mixtures of nitric acid or hyponitric acid with nitrated and other bodies.

Mixtures with an explosive oxidising base—such as charcoal dynamite, and blasting gelatin.

Mixtures formed by oxidising bodies and by oxidisable bodies, none of which is explosive separately—such as powders with a nitrate or chlorate base.

3. The theoretical and practical data which characterise explosive substances having been generally enumerated, as also the practical questions relative to the use, manufacture, and preservation of the same, as well as the proofs of their stability, we have now come to the special study of these matters.

4. We at first treated of gases and detonating gaseous mixtures, beginning with the figures relative to the heat of transformation, at the theoretical gaseous volume and pressure in regard to explosive gases properly so called. Thus, at page 387, we have given the table of the characteristic data respecting the chief gaseous mixtures.

This table indicates that the potential energy of gaseous compounds at unit weight only varies from single to double in the case of gases containing carbon and hydrogen mixed with oxygen. It is also the same in the case of the various hydro-

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carbon gases. But it is far beyond that of all solid or liquid compounds. For instance, in the case of hydrogen and oxygen, the potential energy is four times what it is in ordinary gunpowder, and double what it is in nitroglycerin. In most of the hydrocarbons associated with oxygen it scarcely attains to two-thirds of the energy of an oxyhydric mixture; acetylene alone approaches hydrogen.

But these advantages are discounted by the considerable volume of gaseous mixtures and by the necessity for preserving them in strong receptacles.

We have given the theoretical pressures and the pressures observed for these different mixtures. By comparing these we may observe that the theoretical pressures exceed the real pressures by double and sometimes even more, probably owing to the dissociation of the compounds, water and carbonic acid, and to the increase in the specific heats with the temperature.

In fact, the pressures observed with total combustion mixtures have not exceeded 20 atm., and in most cases they were considerably below the figure. These pressures are very far inferior to those of solid or liquid explosive substances, this inferiority being due to the lesser condensation of the substance.

In the case of liquefied gases, or of analogous bodies, such as hyponitric acid, we obtain a nearer approach to solid substances. The table at page 398 furnishes a certain number of details on this point.

Finally, we have examined the mixtures of gases and combustible dusts to which numerous accidents in mines have been attributed, and we have briefly summarised both the theoretical data and the facts which have come under notice.

5. We now come to liquid or solid explosive compounds. In the case of each of these we have given the physical properties, the temperature of decomposition, the heat liberated, the volume of gases, the permanent pressure, the theoretical pressure at the moment of the explosion, in fact, the results of experiments made recently in order to measure the real pressures and the time necessary for the propagation of the explosion.

6. All these particulars are shown in the following table, which summarises the characteristic details of the principal explosive substances (see next page).

According to this table, gaseous mixtures, such as hydrogen and oxygen, or acetylene and oxygen, represent those systems whose potential energy is the greatest; nitroglycerin and nitromannite, which are the most powerful among solid or liquid powders, do not attain the half of the proportions referred to gases; gun-cotton one-third; potassium picrate slightly over one-fourth, and black powder does not even reach one-fourth.

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Nature of explosive.	Formula.	Weight corresponding to the formula.	Heat liberated at constant volume per kilogramme.	Volume of permanent gas per kilogramme.[1]	Specific pressure according to experiment[2] (1 grm. in 1 c.c.).	Velocity of the explosive wave per second.
		grms.		litres.	atm.	metres.
Oxygen and hydrogen . . .	$H_2 + O$	18	3833 Cal. water liquid[1] 3278 „ „ gaseous	1240	11960	2810
Chlorine and hydrogen . .	$H + Cl$	36·5	603	610	4940	..
Carbonic oxide and oxygen	$CO + O$	44	1483	480	4510	1089
Methane and oxygen . . .	$CH_4 + O_4$	80	2669 Cal. water liquid[1] 2419 „ „ gaseous	840	11420	2287
Acetylene and oxygen . . .	$C_2H_2 + O_5$	106	3001 „ „ liquid[1] 2907 „ „ gaseous	630	8630	2482
Ethylene and oxygen . . .	$C_2H_4 + O_6$	124	2753 „ „ liquid 2592 „ „ gaseous[1]	720	9940	2209
Cyanogen and oxygen . . .	$C_2N_2 + O_4$	116	2263	580	8760	2195
Nitrogen sulphide	NS	46	694	485	8270	..
Nitroglycerin	$C_3H_5(NO_3)_3$	227	1579 Cal. water liquid 1480 „ „ gaseous[1]	713	10950	5000 75 % dynamite
Nitromannite	$C_6H_8(HNO_3)_6$	452	1526 „ „ liquid 1459 „ „ gaseous[1]	692	11500	..
Gun-cotton	$C_{24}H_{12}(HNO_3)_{11}O_9$	1143	1074 „ „ liquid 1022 „ „ gaseous[1]	859	10000	5000 — 6000
Potassium picrate	$C_6H_2K(NO_2)_3O$	267	781	549	$\frac{5600}{n - 0{\cdot}14}$	..
Mercury fulminate. . . .	$C_2HgN_2O_2$	284	463 . . . . . 349 Hg gaseous[3] . .	314	6200 27400[4]	..
Diazobenzene nitrate . . .	$C_6H_4N_2HNO_3$	167	688	818	about 7600	..
Service powder	74·7 nitre 10·1 sulphur 14·2 charcoal 1·0 water	. . .	720–738	278–263	$\frac{2193}{n - 0{\cdot}68}$	..

[1] This represents the reduced volume. In the case where the explosion develops steam, the volume of the latter is comprised in the reduced volume; although, in fact, it is only gaseous at a temperature above 0°, that is to say, that the volume assigned to steam ought to be multiplied by $1 + \frac{t}{273}$, t being the temperature produced at the moment of the explosion. But then the heat liberated should be diminished by the heat absorbed by the evaporation of water. This quantity has been taken, for the sake of simplicity, as equal to 10,000 cal. for 18 grms. of water. The dissociation is also disregarded, the precise data for estimating it being wanting.

[2] This pressure represents the limit towards which the pressures observed at a density of charge $\frac{1}{n}$ (1 grm. of matter in n c.c.) tend, when n tends towards unity. When a non-volatile residuum is produced, the volume of this residuum should be deducted from n; for instance, with black powder and potassium picrate.

[3] Mercury is assumed to be gaseous, that is to say, taken at a temperature over 360°. The real volume is then 314 $(1 + \frac{t}{273})$. The heat liberated has been reduced by the heat of evaporation of mercury.

[4] In its own volume, that is to say, at a density of charge $\frac{1}{n} = 4{\cdot}2$.

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But this inequality is redeemed in practice by the impossibility of raising gaseous mixtures to densities of charge comparable with those of other explosive substances. This observation applies equally to the comparison of the gaseous volumes developed by the two orders of substances. The absolute volume of gases produced by one kgm. of matter is the maximum for hydrogen mixed with oxygen; the other gaseous mixtures scarcely attain the half of this. Among solid or liquid compounds, gun-cotton and diazobenzene nitrate are those which furnish the largest volume of gas, namely, two-fifths of the volume produced by the oxyhydric mixture; nitroglycerin is less by one-sixth; service powder does not attain to one-fourth the volume furnished by the oxyhydric mixture, and is about one-third the volume developed by nitroglycerin or gun-cotton.

Any advantage, however, which gaseous mixtures appear to offer according to these figures is not founded on the actual measurements which have been made of specific pressures. In fact, the most energetic mixtures, such as oxygen and hydrogen, and methane and oxygen, barely attain the same pressures at a given density of charge as nitroglycerin, nitromannite, and gun-cotton, which substances are very similar to one another in this respect.

In truth, the specific pressures are deduced from experiments made with gaseous mixtures at very small densities of charge. Probably, if experimenting with gases compressed beforehand so as to bring them up to densities comparable to those of liquids, we might arrive at much higher specific pressures. At all events the fact is one worth noting.

The specific pressure of black powder under a density of charge equal to unity would exceed the foregoing by about one-half. Mercury fulminate does not go beyond this at this density of charge. But its great specific weight (4·43) allows it to attain four times this pressure when it detonates in its own volume; pressures to which no known body approaches. We have said already that this circumstance plays a leading part in the use of fulminate as a priming.

In order to complete these ideas and to fully characterise explosive bodies, we must further know the duration of the decomposition in each of the substances, that is to say, the specific velocity of their explosive wave. This velocity has, in fact, been found equal to 2840 metres per second in oxyhydric mixtures, and to 2400 metres in acetylene mixed with hydrogen. The other combustible gases give similar velocities, with the exception of carbonic oxide mixed with oxygen, which falls to 1089 metres. With solid or liquid substances similar data are for the most part wanting, nevertheless velocities of 5000 metres have been observed with dynamite, and 5000 to 6000 metres with gun-cotton. These velocities are ample to account for the

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shattering effects produced by these substances. In order to attenuate these effects it is well to dilute the bodies with an inert matter; this tends to change the detonation into a progressive combustion, a phenomenon of quite another character, and in which mechanical actions are exercised more slowly; this kind of combustion is the only one known with any certainty in connection with black powder.

Such are the general results of the comparison of different explosive substances. In this work will be found the theoretical volumes calculated for a great number of other mixtures; but in the above table we have limited ourselves to facts resulting from experiments.

7. Among the interesting conclusions which we have had occasion to develop, attention may be called to the study of the manifold decompositions of the same explosive substance, such as ammonium nitrate; the examination of the properties of nitrogen chloride, of potassium and ammonium chlorate, and of ammonium bichromate; the decomposition of the nitro-ethylic and nitro-methylic ethers; the classification of the various kinds of dynamite and the theoretical discussion of their properties; the study of gun-cotton properly so called, and that of wet, paraffined, and "nitrated" gun-cotton; the examination of picrates, of mixtures formed with nitric acid, associated with an organic matter, and the examination of perchloric ethers, and lastly of oxalates.

8. The study of powders with a nitrate base has led to special developments, both practically and theoretically, owing to the importance of this class of powders.

The chemical reactions which take place between sulphur, carbon, their oxides and their salts, have been carefully studied, as also the decomposition of sulphites and of hyposulphites, and the study of certain charcoals used in the manufacture of gunpowder, and which retain an excess of the original energy of the hydrocarbons from which they are derived. This excess plays a very important part in the explosive properties of gunpowder.

Then the different mixtures of nitre, sulphur, and charcoal which answer to total combustion were examined; the only mixtures in which chemical reaction can be foreseen *à priori*.

Service powders are first studied, taking the products of their combustion such as are known by analysis. After having summarised these analyses and carried them to the fundamental products and to the equivalent relations, the fluctuations observed between these relations are considered, and a theory founded on the existence of five simultaneous equations is established, in accordance with which the metamorphosis is developed in a direction and relative proportion determined by the local conditions of mixture and of inflammation. The

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characteristic data of each of these equations is estimated, and it is shown that they represent all the observed phenomena.

In the case of blasting powder we must also consider the transformation of carbonic acid into carbonic oxide.

Powders with a sodium or barium nitrate base are then considered, but bearing in mind this circumstance, that chemical reactions referred to equivalent weights ought to liberate approximately the same quantities of gas and heat as powder with a base of potassium nitrate, yet that at the same weight sodium nitrate is superior, whereas barium nitrate would be less favourable.

9. We conclude by the examination of powders with a potassium chlorate base, and we show how these powders possess a force superior to those with a base of nitrate, seeing that they liberate more heat and at least an equal volume of gas, but they are very inferior to dynamite and gun-cotton.

They are besides much more dangerous, owing to the extreme facility with which they inflame under the influence of shock or friction, and on account of their shattering properties; the theory of all of which circumstances is accounted for, and which circumstances explain the numerous accidents produced in manufacturing experiments, and the use of chlorate powders made at different periods. Such powders, being also surpassed by dynamite and gun-cotton, do not offer any special advantage to compensate for the exceptional dangers attending their preparation and application.

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TABLE GIVING WEIGHT OF A LITRE OF THE PRINCIPAL GASES.

Names.	Formulæ.	Equivalent weight.	Weight of a litre.
Oxygen	O	8	1·433 (Theory) 1·430 (Regnault)
Hydrogen	H	1	0·08958
Nitrogen	N	14	1·254 (Theory) 1·256 (Regnault)
Chlorine	Cl	35·5	3·18
Bromine	Br	80	7·16
Iodine	I	127	11·18
Sulphur	S	16	2·87
Phosphorus	P	31	2·78
Mercury	Hg	100	8·96
Hydrochloric acid	HCl	36·5	1·635
Hydrobromic acid	HBr	81	3·63
Hydriodic acid	HI	128	5·73
Hydrofluoric acid	HF	20	0·896
Water vapour	H_2O	9	0·806
Hydrogen sulphide	H_2S	17	1·523
Ammonia	NH_3	17	0·761
Hydrogen phosphide	PH_3	34	1·52
Nitrogen monoxide	N_2O	22	1·971
Nitric oxide	NO	30	1·343
Nitrogen trioxide	N_2O_3	38	3·40
Nitric peroxide	NO_2	46	2·06
Sulphurous acid	SO_2	32	2·87
Carbonic oxide	CO	14	1·254
Carbonic acid	CO_2	22	1·971 (Theory) 1·9774 (Regnault)
Hypochlorous oxide	Cl_2O	43·5	3·90
Chlorous oxide	Cl_2O_3	59·5	5·33
Chlorine tetroxide	Cl_2O_4	67·5	3·024
Carbon oxysulphide	COS	30	2·69
Carbon oxychloride	$COCl_2$	49·5	4·43
Acetylene	CH or C_2H_2	13 or 26	1·165
Ethylene	CH_2 or C_2H_4	14 or 28	1·254
Ethane	CH_3 or C_2H_6	15 or 30	1·343
Methane	CH_4	16	0·716
Propylene	C_3H_6	42	1·881
Cyanogen	CN or C_2N_2	26 or 52	2·330
Hydrocyanic acid	HCN	27	1·210

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APPENDIX.

MM. Berthelot and Vieille continued their researches on detonating gaseous mixtures,[1] and their experimental results and their conclusions are embodied in a series of papers published in the "Annales de Chimie et de Physique," 6e série, tom. iv. pp. 3–90; but it is impossible in the space available to give here more than a brief indication of the general character of the communications.

The first is "*On the calculation of the temperatures of combustion, specific heats, and dissociation of detonating gaseous mixtures.*" This is essentially theoretical in character. The second paper is entitled "*Experimental determinations of pressures,*" and the third relates to the "*Relative rapidity of combustion of various gaseous mixtures.*" The fourth is on the "*Influence of the density of gaseous mixtures on the pressure, and isomeric mixtures.* The experiments were made both with gaseous mixtures compressed beforehand and with isomeric mixtures.

The remaining four papers are theoretical, and treat of the *Calculation of the temperatures and specific heats of gaseous mixtures; the specific heats of gaseous elements at very high temperatures; the specific heats of water and carbonic acid at very high temperatures;* and finally, in the last paper, M. Berthelot examines the manner in which the consequences which result from the experiments affect two fundamental questions—*the scale of temperatures* and that of the *molecular weights.*

The following results are taken from the second paper, on the *determinations of pressures*:—

First Group.—Hydrogen Mixtures.

I. *Hydrogen and oxygen.*

	Pressures. atm.
(1) $H_2 + O$	9·80
(2) $H_2 + O + H_2$	8·82
(3) $H_2 + O + 2H_2$	8·02
(4) $H_2 + O + 3H_2$	7·06
(5) $H_2 + O + O_2$	8·69
(6) $H_2 + O + 3O_2$	6·78

[1] p. 383.

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	Pressures. atm.
II. *Hydrogen, nitrogen, and oxygen.*	
(7) $H_2 + O + \frac{1}{2}N$	9·16
(8) $H_2 + O + N_2$	8·75
(9) $H_2 + O + 2N_2$	7·94
(10) $H_2 + O + 3N_2$	6·89
III. *Hydrogen and nitrogen monoxide.*	
(11) $H_2 + N_2O$	13·60
(12) $H_2 + N_2O + N_2$	11·08

SECOND GROUP.—OXYCARBONIC MIXTURES.

I. *Carbonic oxide and oxygen.*	
(13) $CO + O$	10·12
II. *Carbonic oxide, nitrogen, and oxygen.*	
(14) $CO + N + O$	9·33
(15) $CO + N_2 + O$	8·77
(16) $CO + 5N + O$	7·05
III. *Carbonic oxide and nitrogen monoxide.*	
(17) $CO + N_2O$	11·41
IV. *Varied mixtures.*	
(18) $2CO + H_2 + O_2$	9·81
(19) $2CO + H_4 + O_4$	8·79
(20) $2CO + H_2 + O_3$	9·44
(21) $2CO + H_3 + O_4$	9·61

THIRD GROUP.—CYANOGEN.

I. *Cyanogen and oxygen; total combustion.*	
(29) $C_2N_2 + O_4$	20·96
II. *Cyanogen, nitrogen, and oxygen; total combustion.*	
(30) $2C_2N_2 + 2N_2 + O_5$	17·70
(31) $C_2N_2 + 2N_2 + O_4$	14·74
(32) $C_2N_2 + 4N_2 + O_4$	12·33
III. *Cyanogen, nitrogen, and oxygen; incomplete combustion.*	
(33) $C_2N_2 + O_2$	25·11
(34) $C_2N_2 + 1\frac{1}{2}N + O_2$	20·67
(35) $C_2N_2 + 2N_2 + O_2$	15·26
(36) $C_2N_2 + 2\frac{1}{2}N_2 + O_2$	11·78
IV. *Cyanogen, carbonic oxide, and oxygen; incomplete combustion.*	
(37) $2C_2N_2 + 1\frac{1}{2}CO + O_4$	21·24
(38) $C_2N_2 + 2CO + O_2$	15·46
V. *Cyanogen and compound combustive gases; total combustion.*	
(39) $C_2N_2 + 4NO$	16·92
(40) $C_2N_2 + 4N_2O$	22·66
VI. *Cyanogen and compound combustive gases; incomplete combustion.*	
(41) $C_2N_2 + 2NO$	23·34
(42) $C_2N_2 + 2N_2O$	26·02

This last is the greatest pressure which has been obtained with gaseous mixtures taken at the normal pressure.

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FOURTH GROUP.—HYDROCARBONS.

I. *Pure gases.*

	Pressures. atm.
(22) Acetylene, $C_2H_2 + O_5$	15·29
(23) Ethylene, $C_2H_4 + O_6$	16·13
(24) Ethane, $C_2H_6 + O_7$	16·18
(25) Methane, $2CH_4 + O_8$	16·34

II. *Varied mixtures..*

(26) Ethylene and hydrogen, $C_2H_4 + H_2 + O_7$ ...	14·27

III. *Gases containing oxygen.*

(27) Methylic ether, $C_2H_6O + O_6$	19·91
(28) Ordinary ether, $C_4H_{10}O + O_{12}$	16·33

In regard to the *relative rapidity of combustion of various detonating gaseous mixtures*, the authors found that in the total combustion of hydrogen, carbonic oxide, cyanogen, and hydrocarbons containing much hydrogen, by oxygen and nitrogen monoxide, the rate of combustion was much slower with carbonic oxide than with hydrogen. The use of nitrogen monoxide in place of oxygen retarded the action, and the rapidity of combustion of cyanogen and the hydrocarbons was little different from that of hydrogen.

In the case of incomplete combustion of cyanogen the rate was more rapid than when the combustion was complete.

Experiments on the influence of an excess of one of the components, hydrogen or oxygen, showed that in both cases the combustion was retarded, the retarding effect of the oxygen, however, being nearly double that of the hydrogen for equal volumes.

The presence of products of combustion also caused great retardation, the rate being three times slower for an equal volume of carbonic acid, and six times for carbonic oxide. An inert gas, such as nitrogen, retards the combustion of hydrogen more than that of carbonic oxide. This shows that the phenomenon is not only due to the lowering of temperature, which is approximately the same in both cases, but also to the greater inequality between the velocities of translation of the gaseous molecules.

Combustion proceeds more slowly in the less condensed isomeric systems.

When two combustible gases, such as hydrogen and carbonic oxide, are burned with oxygen, the rate is in no case the mean of that of the two gases. They appear to burn separately each with its own rapidity.

The fact that the rapidity of combustion of hydrocarbons rich in hydrogen is nearly the same as that of hydrogen appears to indicate that the hydrogen burns before the carbon, even in total combustions.

From their experiments on the *influence of the density of detonating gaseous mixtures on the pressure* the authors find that the results do not differ much from those calculated according to the ordinary laws of gases, but have the advantage of being independent of the laws themselves. They conclude that at

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about the highest temperatures known, 3000°–4000° on the air thermometer:

(1) The same quantity of heat being supplied to a gaseous system, the pressure of the system will vary in proportion to its density.

(2) The specific heat of gases is practically independent of the density as well at high temperatures as at 0°.

(3) The pressure increases with the quantity of heat supplied to the same system.

(4) The apparent specific heat increases with this quantity of heat.

Referring to temperatures deduced from the expansion of a given volume of air, M. Berthelot points out that the scale of temperatures defined by the variations in volume at constant pressure (or by the variations in pressure at constant volume) and the scale of temperatures defined by the quantities of heat absorbed will correspond between 0° and 200°, but will diverge more and more as the temperature increases until when the temperature deduced from the expansion indicates 4500°, that calculated from the heat absorbed will be 8815°.

Further, he says that the indications of an air and of a chlorine or iodine thermometer differ greatly at high temperatures, and that there is no valid reason for preferring the indications of an air thermometer to those of a chlorine thermometer in the definition of temperatures.

The rapidity of propagation of detonation in solid and liquid explosives.

In continuation of the experiments made with gaseous mixtures while studying the explosive wave (p. 88), M. Berthelot, with the assistance of members of the French Explosive Commission, has extended his experiments to solid and liquid explosives. Full details are to be found in "Annales de Chimie et de Physique," 6e série, tom. vi. pp. 556–574. Trials were made with gun-cotton and "starch powder" compressed in metallic tubes, and at different densities of charge; also on granulated gun-cotton, dynamite, liquid nitroglycerin, and panclastite, a mixture formed of equal parts of carbon disulphide and liquid nitric peroxide.

I. Compressed Gun-cotton.

(1) In a former series of experiments the velocity in *leaden tubes* 4 mm. exterior diameter, and about 100 m. in length, varied

from 3903—4267 m. per second,
and from 4818—6238 m. per second

in *tin tubes* of the same size. The density of charge, however, was 1·4 in the tin tubes, and varied from 0·9 to 1·2 in the lead tubes. This may have occasioned the variation in velocity.

(2) In a second series of experiments, made a few years afterwards on similar gun-cotton, at densities of charge varying from

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1 to 1·2, contained in *leaden tubes* 4 mm. external diameter, and about 100 m. in length, the average velocity varied from

4952 m.—9500 m. (9 experiments),

and from 4749 m.—5133 m. for similar tubes covered with plaited string.

In a similar tube the velocity measured at successive intervals of 25 m. varied from

4671 m.—5980 m.,

being least at the beginning.

The general average of the velocities is

5200 m.

The irregularity of the results appears to be due to the difficulty of obtaining leaden tubes of uniform internal diameter. The duration of the phenomenon may also be influenced by the time necessary to destroy the tubes. To get perfectly regular results it would be necessary to have tubes which would not burst. This has only been accomplished when working with gaseous systems.

(3) With the same product contained in a tin tube, the density of charge being slightly higher, that is over 1·2, the average velocity varied

from 5736 m.—6136 m. for tubes of 4 mm. external diameter, and from 5845 m.—6672 m. for tubes of 5·5 mm. diameter.

II. Nitrohydrocellulose.

		Velocity per second.
(25 m.) from 2nd to 3rd interrupter	... ...	6389 m.
(25 m.) „ 3rd to 4th „	... ...	5932 „
(25 m.) „ 4th to 5th „	... ...	6435 „
	Mean velocity	6242 m.

Experiments were also made in a tin tube, consisting of two parts, one 4 mm., the other 5·5 mm. in diameter. The general average velocity in the 4 mm. tube was

4919 m.

and in the 5·5 mm. tube 6100 m.

Apparently the velocity was rather more rapid in the tin tubes (5916 m.) than in the leaden ones (5200 m.); perhaps because the former metal resists longer than the latter the explosive effort which destroys the tube.

III. Granulated Gun-cotton.

At high density of charge, 1·17, in a tube 2 mm. internal diameter, the average velocity was

4770 m.

In a tube 3·15 mm. internal diameter, density of charge 1·27, the mean velocity was

5406 m.

This greater velocity was due to the greater diameter of the tube and density of charge.

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At low densities of charge, 0·67 and 0·73, the mean velocities varied from

3767 m. to 3795 m.

This reduced velocity is evidently occasioned by the greater discontinuity of the explosive resulting from the diminished density of charge.

Abel, operating with dry compressed gun-cotton placed in continuous trains in the open, observed velocities of

5320 m. to 6080 m.

with gun-cotton containing 20 per cent. of water—

6090 m.

with "nitrated" gun-cotton—

4712 m. and 4865 m.

With charges of gun-cotton placed in an iron tube and separated by spaces of 1 mm., he found

1800 m.,

the transmission being retarded on account of the discontinuity

IV. "Starch" Powder.

The average velocities observed with this powder, density of charge about 1·2 in a tin tube 4 mm. external diameter, were in two experiments 5222 m. and 5674 m.

In a tin tube 5·5 mm. external diameter, the velocity was 5816 m.

In a leaden tube, for density of charge between 1·1 and 1·2, the average velocity was 5006 m., and for 1·35 density 5512 m. All other things being equal, the velocity increases with the density of charge. The process employed for making these tubes does not permit of the interior diameter being sufficiently guaranteed to authorise definite conclusions being drawn from the difference in velocities observed in tubes of tin and lead.

V. Nitromannite.

Compressed pulverulent nitromannite fired in leaden tubes 4 mm. external diameter, density of charge 1·58 and 1·53, gave average velocities of 6911 m., 7082 m., and 6965 m. At higher density of charge, 1·9, the average velocity was 7705 m.; and this is the highest average velocity which has been observed.

VI. Nitroglycerin.

Liquid nitroglycerin detonates with difficulty in narrow tubes at low temperature, it having been found impossible to detonate it in a leaden tube of less than 3 mm. diameter at 12° to 13°.

In tubes of lead or Britannia metal of 3 mm. to 4 mm. diameter, temperature 14°, when placed in the shade, the detonation was only transmitted a short distance; but when the tubes were placed in the sun, and thereby heated to 18° to 20°, the detonation was transmitted the whole length of the tube.

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This difference is apparently due to the greater viscosity of the liquid at lower temperatures.

Average velocities of 1310 m., 1015 m., and 1286 m. were observed in lead, Britannia metal, and tin tubes 3 mm. in diameter. A Britannia metal tube 9 mm. in diameter gave 1386 m. Abel found 1672 m. under slightly different conditions.

VII. Dynamite.

Velocities of 2333 m. and 2753 m. were observed in Britannia metal tubes 3 mm. internal diameter, while in tubes of the same metal or lead 6 mm. diameter the average velocity was 2668 m.

Abel found 5928 m. to 6566 m. for a train of dynamite cartridges, 30 mm. in diameter, placed end to end and fired in the open air. These much higher velocities are no doubt due to the much greater diameter of the explosive cylinders.

VIII. Panclastite.

Owing to the extreme volatile nature of this mixture, bubbles of gas formed in the interior of the tube, and caused irregularity in the results. A mixture of equal parts of liquid nitric peroxide and carbon disulphide, contained in a leaden tube 3 mm. internal diameter, gave 4685 m. velocity; another similar experiment gave 5470 m. in the first half of the tube, and 6658 m. for the total length. On the whole, these figures are similar to those found for gun-cotton.

To sum up, principally from the experiments made with gun-cotton—

The velocity increases with the density of charge. It increases with the diameter, at least within the limits of the very narrow tubes experimented with.

It appears to increase with the resistance of the envelope (the latter being pulverised by the explosion).

Finally, comparative measurements made with a tube of 200 mm. very much curved, and a similar but straight tube, gave practically the same velocity.

These experiments should be regarded as applicable to practical conditions comparable to those under which they were made, although the indications of the correlation between the velocity and the density of charge or the resistance of the envelopes appear conformable to theory.

To further develop this study, experiments were made with a homogeneous and very mobile liquid explosive, methyl nitrate (p. 420), contained in tubes of caoutchouc, glass of different thicknesses, Britannia metal, and steel.

The details of these experiments are to be found in a communication on the "Explosive Wave," by M. Berthelot, "Annales de Chimie et de Physique," 6e série, tom. xxiii. pp. 485–503 (1891).

1. *Canvas-covered caoutchouc tubes.*—The tube had an internal

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diameter of 5 mm., the external diameter being 12 mm. and the length 39·8 m. The velocity was found to be 1616 m. per second. The tube after the explosion was rent in long plates in the direction of the length of the tube.

2. *Glass tubes.*—Numerous experiments were made, but the results were not very concordant. The following are extreme numbers:—

Internal diam.	Thickness.	Velocity per second.
3 mm.	4·5 mm.	2482 m.
3 „	2·0 „	2191 „
3 „	1·0 „	1890 „

The thinnest glass tube resisted longer than the canvas-covered caoutchouc, but the glass tubes were pulverised in every case by the explosion.

3. *Britannia metal tubes.*—Experiments made with tubes 3 mm. internal and 6 mm. external diameter, and about 50 m. long, all in one piece, showed an average velocity of 1217 m. This metal offers less resistance and breaks more quickly than the thinnest glass and canvas-covered caoutchouc.

4. *Steel tubes.*—Specially drawn steel tubes, in uniform lengths of 5 m., were obtained which had been very carefully annealed by heating in a closed vessel for 42 hours, in order to prevent all crystalline structure. The internal diameter was 3 mm. and the external 15 mm.

Experiments were made in tubes about 20 m. long, formed of four lengths carefully joined together in a special manner.

Average velocities of 2155 m. and 2094 m. were observed. All the steel tubes operated with, opened during the explosion, and were split into long plates as in the caoutchouc tubes.

The fracture of such thick steel tubes shows that there is no hope of being able to detonate a liquid explosive in a metallic tube in its own volume without breaking it, whatever be the thickness of the tube. This is explained by the fact established by the theory of elasticity, that the resistance of a metallic tube does not increase indefinitely with its thickness. The resistance tends towards a certain limit beyond which the walls of the vessel tear whatever be the thickness. Now explosive liquids, like methyl nitrate, offer this remarkable property—that *the volume defined by their density is less than the volume limit* below which the gases or liquids produced by the explosion are susceptible of being reduced by the pressure developed in the limits of the experiments.

It is known that gases cannot be indefinitely reduced in volume by compression, their compressibility diminishing beyond certain limits. This is still more the case with solids and liquids, the volumes of which cannot be materially altered by pressure. Suppose, for instance, that the gases produced by the explosion of methyl nitrate—carbonic acid, carbonic oxide, nitrogen, gaseous water—at about 3000°, the temperature developed by the explosion, tend towards a density near unity; then the possible volume of the gas will be about one-fifth greater than that of the methyl nitrate (density 1·182). Consequently the vessel will necessarily be ruptured before the whole of the matter has detonated, and

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this will take place at a moment which will vary with its own instantaneous resistance. This resistance is quite different from the static resistance of the vessel, which can be measured by hydraulic pressure.

Let us examine what actually happens when an explosive detonates in a tube, the detonation being provoked in the first instance by the violent shock of the mercury fulminate, which immediately raises to the extreme limit the initial pressure, the heat which it disengages, and the chemical reactions developed from layer to layer which arise from it.

No regular state of affairs corresponding to the explosion of the matter in its own volume can be established, since the tube is necessarily broken. However, if it be homogeneous, so that the pressures and reactions can be propagated in a uniform manner, then the tube will be regularly and progressively ruptured in proportion as the pressure propagated attains a certain limit, and thus a special *régime* of detonation may be established which will depend on the conditions realised in the system. A velocity of propagation fairly uniform for each given system will then be observed, but very variable between different systems even when the same explosive has been used, as shown by the experiments with methyl nitrate and the tubes of different material.

This *régime* of detonation depends on the structure of the explosive as well as on the nature of the envelope. Thus nitroglycerin gives a lower velocity than dynamite, it being a viscid liquid which transmits the shock which determines detonation more irregularly than the silica uniformly impregnated with it. Dynamite made with mica gives still higher velocities, which is accounted for by the crystalline structure of the mica, this body being more rigid than the amorphous silica. This view is also confirmed by the observations made with nitromannite, a solid crystalline body, which appears more apt to transmit the detonation than liquid methyl nitrate, having given a velocity of 7700 m.; picric acid, another crystalline body, has given 6500 m. This contrast between liquid methyl nitrate and crystallised nitro compounds is thus in accord with what has been observed between nitroglycerin and dynamite.

On the other hand, in certain pulverulent systems in which complete continuity has almost been attained by compression, experiment has proved that there is a limit of compression beyond which the mass cannot be exploded by a fulminate detonator. This has been observed with certain powders formed of potassium chlorate and tarry materials.

A few further observations with gun-cotton may be given as showing the influence of the envelope.

Compressed gun-cotton, density of charge 1 and 1·27, gave velocities of 5400 m. in leaden tubes of 3·15 mm. internal diameter; while with density of charge 0·73, in a leaden tube 3·77 mm. internal diameter, the velocity observed was 3800 m., the inequality being evidently due to the less continuity of the material. The feeble resistance of the envelope may be compensated by the mass of the explosive, which prevents, especially

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in the centre, the instantaneous escape of the gases. This is shown by Abel's experiments, already referred to, when he observed velocities of 5300 m. to 6000 m.

The facts set forth in this paper show that the explosive wave only exists with its simple characteristics and definite laws, in the detonation of gases. These laws and characteristics only partially hold in the detonation of liquids and solids while remaining subject to the same general notions of physico-chemical dynamics.

On the different modes of explosive decomposition of picric acid and nitro compounds.[1]

Considerable diversity of opinion has existed as to whether picric acid can be exploded by simple heating. It is indeed much less explosive than nitric ethers like nitroglycerin and gun-cotton, for if a fairly large mass be heated gradually in a capsule or flask it melts and emits vapours which catch fire and burn with a fuliginous flame, but without giving rise to any explosion. A very small quantity carefully heated in a glass tube may even be volatilised without decomposition.

But it is a mistake to believe that picric acid is incapable of exploding by simple heating. Now this body, when submitted to a high temperature, decomposes with disengagement of heat, oxidising itself at the expense of the nitrous vapours it contains. The author has experimentally proved that when a reaction liberates heat its rapidity increases, on the one hand, with the condensation of the matter for the same temperature, and, on the other hand, with the temperature for the same condensation. The latter increase takes place very rapidly, according to a law expressed by an exponential function of the temperature. This tends to render the reaction explosive.

When a closed vessel is used the heat disengaged by the reaction helps further to elevate the temperature, and consequently to accelerate the phenomena.

In conformity with these principles picric acid may be caused to detonate violently in an open vessel at the ordinary pressure, when it is suddenly heated in a vessel which has been previously raised to a high temperature, and the mass of which is such that the introduction of a small quantity of picric acid does not appreciably modify the general temperature.

The experiment may be made in the following way:—A glass tube is taken, closed at one end, and about 25 mm. or 30 mm. in diameter, placed vertically over the flame of a gas burner, and heated to visible redness, without, however, melting the tube. Two or three crystals of picric acid, not exceeding a few milligrams in weight, are projected into the bottom of the tube, when they immediately explode violently, before having had time to be reduced to vapour, a very bright white light and characteristic noise being also produced.

An experiment was made in an atmosphere of nitrogen, and only a few flakes of carbon remained.

[1] "Annales de Chimie et de Physique," 6e série, tom. xv. pp. 21-25.

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If a larger quantity, not more, however, than a few centigrams, be used, the bottom of the tube may be sufficiently cooled to prevent immediate detonation, but the picric acid will be vaporised and a less violent explosion, accompanied with flame, will soon take place.

With a decigram of the acid the action is slower, but the substance soon fuses and deflagrates with vivacity. Finally, if the quantity be still further increased, the acid decomposes without deflagration.

Similar experiments were also made on other nitro compounds, and it was found that nitrobenzene, dinitrobenzene, mono-, di-, and trinitronaphthalene all detonated under the conditions of the experiments, while giving rise to different modes of decomposition when the quantities were increased.

These varied modes of decomposition[1] depend on the initial temperature of decomposition.

If the surroundings be of sufficient mass to absorb the heat produced there will be neither deflagration nor detonation. If, however, a large mass of a nitro compound like picric acid while burning heats the walls of the vessel containing it sufficiently to start deflagration, this will still further heat the containing vessel, and the phenomenon may develop into detonation.

It would suffice, if this happened at an isolated point, through a fire or any local superheating, to start the explosive wave, which would be propagated through the entire mass, and thus give rise to a general explosion.

[1] Compare the different modes of decomposition of ammonium nitrate, p. 5.

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